

Novel catalysts for chemical CO2 utilization

Radoslaw Dębek

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AGH University of Science and Technology Faculty of Energy and Fuels University of Pierre and Marie Curie Institut Jean Le Rond D'Alembert

PhD Thesis

Novel catalysts for chemical CO₂ utilization

Nowe katalizatory do chemicznej utylizacji CO₂

Design de nouveaux catalyseurs pour la valorisation chimique de CO₂

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Kraków 2016

Oświadczam, świadomy odpowiedzialności karnej za poświadczenie nieprawdy, że niniejszą pracę doktorską wykonałem osobiście i samodzielnie oraz iż nie korzystałem ze źródeł innych niż wymienione w pracy.

Radosław Dębek

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LIST OF ABBREVIATIONS

- AC Activated Carbon
- ACE Anion Exchange Capacity
- ATR Autothermal Reforming of methane
- CCS Carbon Capture and Storage
- CCU- Carbon Capture and Utilization
- CETS Chemical Energy Transmission and Storage
- CLC Chemical Looping Combustion
- CNs Carbon Nanotubes
- CP co-precipitation
- DEA diethanolamine
- DFT Density Functional Theory
- DME dimethyl ether
- DRIFT Diffuse Reflectance Infrared Fourier Transformation
- DRM Dry Reforming of Methane
- ECBM Enhanced Coalbed Methane Recovery
- EGR Enhanced Gas Recovery
- EOR Enhanced Oil Recovery
- FAMEs Fatty Acid Methyl Ethers
- FT Fischer Tropsch Synthesis
- FTIR Fourier Transform Infrared Spectroscopy
- GHG Greenhouse Gases
- GHSV Gas Hourly Space Velocity
- GTOE Giga tonnes of Oil Equivalent
- HC Hydrocarbons
- HFCs hydrofluorocarbons
- HTs Hydrotalcites
- IGCC Integrated Gasification Combined Cycle
- **IMP** Impregnation
- LDHs Layered Double Hydroxides
- MDEA methyldiethanolamine
- MEA Monoethanolamine
- MeOH methanol
- MTBE Methyl tetr-buthyl ether
- MTG methanol to Gasoline
- MTO Methanol to Olefins
- NP nanopolyhedra
- NR nanorods

- OCM Oxidative Coupling of Methane
- ODH Oxidative Dehydrogenation
- OM Oxidation of methane
- PFCs perfluorocarbons
- POM Partial Methane Oxidation
- PSA Pressure Swing Adsorption
- RWGS Reverse Water Gas Shift
- SEM Scanning Electron Microscopy
- SERP Sorption Enhanced Reaction Process
- SRM Steam Reforming of Methane
- STP Standard conditions of temperature and pressure
- TEM Transmission Electron Microscopy
- TG Thermogravimetry
- TOF Turnover Frequency
- TOS Time On Stream
- TPD Temperature Programmed Desorption
- **TPR Temperature Programmed Reduction**
- **TPSE** Total Primary Energy Supply
- TRM Tri-Reforming of Methane
- TSA Temperature Swing Adsorption
- WGS Water Gas Shift
- XRD X-ray diffraction
- XRF X-ray Fluorescence

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1. Introduction

Carbon dioxide emissions are growing with every year. In 2014 they reached record value of 35.9Gt. Such high emissions forced governments to implement CO₂ emissions reduction strategies. European Union set the long-term goal of reducing greenhouse gas emissions by year 2050 by 80-95% with respect to the 1990 levels. This goal may be realized by the implementation of different technologies aiming either at capture and storage (CCS) or capture and utilization (CCU) of carbon dioxide. The CCS technologies have a limited capacity and fossil fuels are predicted to be still the main source of energy in the coming decades. Thus, the chemical utilization of CO₂ is a key element for sustainable development towards low-carbon economy. The application of CO₂ as chemical feedstock allows to deal with the emissions problem in a more active way by CO₂ recycling into added-value products, such as e.g. synthetic fuels. Additionally, the application of CCU technologies may change the image of CO₂, by proving that it is a valuable chemical and an important source of carbon with almost zero costs of production.

Dry reforming of methane (DRM) has been considered during the past decades as a prospective process for the valorisation of carbon dioxide, yielding a syngas with equimolar H₂/CO ratio, suitable for its direct use in different chemical reactions, such as Fischer-Tropsch synthesis, or the production of oxygenated compounds. Nickel-containing catalysts have been presented as a promising alternative to noble metal based ones, as they are cheaper and nickel is more available material than noble metals. The main issue concerning Ni-based catalysts for DRM process is their fast deactivation, due to the formation of coke deposits, sintering or oxidation of active phase. There is therefore a need to develop low-cost, active and stable catalysts, in order to introduce DRM process on industrial scale.

The proposed strategies towards increasing stability of nickel-based catalysts include the application of different supports and/or promoters aiming at increasing interactions between support and active nickel phase. Basing on available literature concerning nickel-based catalysts for dry methane reforming, it is possible to distinguish a few supports which positively influence catalysts activity and stability. Nickel supported on alumina showed good catalytic properties and resistance to coke formation, which was attributed to the formation of spinel phase NiAl₂O₄ and thus increased interactions between nickel and support. In this way nickel resistance to sintering is increased, as well as the formation of carbon deposits is inhibited, because such formation is favoured on large Ni crystallites. Another support, which showed beneficial effect on catalyst performance is magnesia. The positive effect of magnesia is attributed to the ability of the formation of solid solution with NiO at any ratios, thus increasing interactions between active phase

and support. Moreover, MgO possesses high basicity which enhances CO₂ adsorption on the catalyst surface and, as a consequence, may lead to oxidation of carbon deposits via reverse Boudouard reaction. Some authors suggest that the application of Ni catalyst supported on mixed magnesia-alumina have more beneficial effects than application of such single supports. Another important issue are promoters for DRM process. As promoters metal oxides with basic or redox properties are considered. E.g. ceria, due to its high oxygen storage properties, have been proven to increase the stability of catalysts for DRM, when applied as promotor or support.

Among different materials applied for DRM, the catalysts obtained through the thermal decomposition of layered double hydroxides, i.e. hydrotalcites, have been reported to show interesting catalytic performance over long-run catalytic tests. The beneficial influence of application of HTs-derived catalysts comes from the unique properties of such precursors. Firstly, the composition of hydrotalcites may be strongly controlled and, to certain extent, designed to contain desired elements, e.g. NiO, MgO, Al₂O₃. Moreover, the introduction of different type of species into hydrotalcite structure guarantees homogenous distribution, as cations are randomly distributed in the brucite-like layers. The products of thermal decomposition of hydrotalcites exhibit basic properties, desired in DRM reaction, and so called 'memory effect' i.e. ability of reconstructing layered structure, which gives another route of materials modification.

The research on hydrotalcite-derived Ni-containing catalysts for DRM has gained much attention during last decade, especially last 3-4 years, which is directly reflected in the number of papers concerning such catalysts for methane dry reforming. Nevertheless, there are still a lot of uncertainties and questions which need to be addressed, concerning:

- the effect of nickel loading in brucite-like layers,
- new methods of nickel introduction, or
- the effect of different promoters, such as Zr and/or Ce.

The main goal of this PhD thesis was to fill these gaps. The assumed thesis was that by the implementation of varied modification techniques, different promoters and different Ni/Mg/Al ratios for hydrotalcite-derived catalysts, it is possible to tailor the properties of such catalysts and therefore establish optimal composition and preparation procedure to obtain an active, selective and stable catalyst for DRM reaction. The studies presented in this thesis confirmed such hypothesis.

2. Aim of this PhD thesis

The aims of this PhD thesis were to:

- prepare hydrotalcite-derived catalysts containing nickel, characterize them by various techniques in order to establish their physico-chemical properties and subsequently test them in the reaction of dry reforming of methane.
- check the influence of the method of nickel introduction into hydrotalcite-based catalytic system on catalytic properties of the prepared materials.
- establish the optimal composition of Ni-containing hydrotalcite-derived catalyst (Ni/Mg/Al molar ratio) for the DRM reaction.
- establish the influence of promoters, ceria and zirconia, on the catalytic properties of hydrotalcite-derived catalysts.

The realization of these goals/aims allowed to prove the assumed hypothesis that the modification of hydrotalcites (application of different preparation techniques and application of promoters-Ce and/or Zr) allows to tailor catalytic properties of HT-derived materials in dry reforming reaction, and that the appropriate composition of catalyst precursor (Ni/Mg/Al molar ratio) allows to optimize catalyst activity and selectivity in DRM reaction.

3 Chemical utilization of carbon dioxide

The growing concerns about global climate change and increasing social awareness of the environmental problems have created a need for more sustainable development. Thus, our society needs to face new challenges, such as mitigation of climate change, preservation of the environment, usage of renewable energy and replacement of fossil fuels. The realization of these challenges requires new breakthrough solutions in order to be successfully addressed. There is no doubt that carbon dioxide (CO₂) is a common factor in these great challenges. The increasing emissions of this greenhouse gases (GHG) are of large concern and therefore nowadays a huge effort is dedicated to reduce emissions of GHG, especially carbon dioxide, which contributed in total to ca. 75% of 49 GtCO₂eq (in 2010) GHG emissions (Fig. 3.1 A) [1].

3.1 CO₂ emissions

Carbon dioxide emissions have been constantly growing worldwide since pre-industrial era reaching the level of 35.9 Gt in 2014 [2]. This caused the increase of CO_2 concentration from ca. 280 ppm (parts per million) in the mid-1800s to 397 ppm in 2014, with an average growth of 2 ppm/year in the last 10 years [3]. More than 60% of anthropogenic greenhouse gas emissions, for which over 90% is associated with CO₂, are coming from energy sector. Between 1971 and 2013 an increase by 150% in global total primary energy supply (TPSE) has been observed, which is mainly caused by worldwide economic growth and development. Although for last few decades a huge development of renewable and nuclear energy sources was observed (which are considered nonemitting sources of energy), the world energy supply was relatively unchanged over past 42 years and fossil fuels still account for ca. 82% (in 2013) of world primary energy supply [3]. Therefore, carbon dioxide emissions are strongly associated with the combustion of fossil fuels (Fig. 3.1 B). Two fuels which accounted for the highest CO_2 emissions are coal and oil. Till early 2000s the shares of oil in global CO₂ emissions was exceeding those from coal. The situation changed in the beginning of 2000s, due to the higher consumption of coal by developing countries, such as India and China, where energy-intensive industrial processes are growing rapidly and large coal reserves are present.

Power plants, petrochemical and chemical industry and cement industry are currently considered as the main sources of carbon dioxide emissions [4]. However, electricity and heat generation accounted for 42% of global CO₂ emissions in 2013, making it the highest emitting sector (Fig. 3.1 C) [3]. Such high emissions from energy and heat generation are associated with high consumption of coal, which has the highest carbon content per unit of energy released with respect

to other fossil fuels. This trend is foreseen to be the same for the coming years, as many countries, such as Australia, China, India, Poland and South Africa produce over two thirds of electricity and heat from the combustion of fossil fuels [3].



Fig. 3.1 The greenhouse gas emissions and CO₂ emissions: (A) global greenhouse gas emissions in 2010 by gas [1]; (B) global CO₂ emissions by fuel in 1980-2013 [5]; (C) global CO₂ emissions by sector in 2013 [3]; global CO₂ emissions in 1980-2013 by region [5].

The CO₂ emissions of energy production by country or region are dependent on the geopolitical situation, economy, type of fuel and energy mix. However, it is important to underline that top 10 emitting countries (China, USA, India, Russia, Japan, Germany, Korea, Canada, Iran and Saudi Arabia) account for two thirds of global CO₂ emissions [2, 3, 6]. The region of highest CO₂ emissions is Asia (mainly China and India) (Fig. 3.1 D). In 2014, China increased its CO₂ emissions only by 0.9% with respect to 2013, which was the lowest annual increase observed in the last 10 years. The United States (second biggest emitter of CO₂) also showed increase of CO₂ emissions by 0.9% in 2014, which is lower than in the previous 2 years and was associated with a decrease in coal-fired power generation and increased consumption of natural gas. In 2014, the European Union continued to decrease emissions of CO₂ and due to the decrease in fossil-fuel consumption for power generation and lower demand for space heating, the EU-28 decreased the total CO_2 emissions by 5.4% [6].

3.1.1 Reduction of CO₂ emissions – policies

It is important to understand global driving factors of CO₂ emissions in order to find effective solutions for reduction of GHG emissions. The growing world population and demand for energy, as well as practically unchanged carbon intensity of the energy mix, caused drastic increase of CO₂ emissions during last two decades. It is well known that the high increase of emissions of greenhouse gases to the atmosphere in the last 150 years was caused mainly by well-developed countries, which emitted high amounts of GHG during industrial era. These countries in general apply today a greenhouse gas emissions reduction policies, which are resulting in decreasing emissions. However, at the same time, currently developing countries emit enormous amounts of GHG. This is mainly caused by differences in economic, demographic and technological levels. Thus, in order for the world to develop in the sustainable way, the efforts must be undertaken by all countries.

The first international agreement which forced reduction of GHG emissions was Kyoto Protocol linked to the United Nations Framework Convention on Climate Change, adopted in 1997 and entered into force in 2005. In general, Kyoto Protocol stated that industrialised countries were required to reduce GHG emissions (CO₂, CH₄, N₂O, HFCs, PFCs, SF₆) on average by 5% against 1990 levels during the years 2008-2012 (first commitment period). The specific levels of reduction differed for each participating country depending on political and economic situation, i.e. targets for Poland, France, Germany and European Union were equal respectively, -6, 0, -21 and -8% [7]. The second commitment period (years 2013-2020) requires to reduce GHG emissions by at least 18% with the respect to 1990 levels. In order to bring Kyoto's Protocol second commitment period into force, it requires ratification by two-thirds of participating countries (144 countries). Till 1st October 2015 only 49 countries have ratified Kyoto Protocol, and some of the biggest emitters did not participate in it (United States), requires that new international agreements are established.

In December 2015, in Paris, during COP21 (United Nations Conference on Climate Change) a new international climate agreement was finalised which will be applied from 2020. This agreement assumes the participation of both developed and developing countries. The goal is to limit global temperature increase to less than 2°C above industrial levels, which will be realised by reduction of GHG emissions [8]. European Union has been applying different GHG emission reduction policies for several years now, which resulted in the decrease of total CO₂ emissions by 0.4, 1.4 and 5.4%, respectively in 2012, 2013 and 2014 [6]. These achievements were reached thanks to the implementation of 20/20/20 policy which sets the following targets for year 2020 [9]: (i) reduction of greenhouse gas emissions by 20%, (ii) the share of renewable energy at the level of at least 20%, and (iii) improvements in energy efficiency by 20%. In 2014 a new policy was accepted for the period of 2020-2030, which set new targets for 2030 year: (i) the reduction of GHG emissions by 40% with respect to 1990 level, (ii) at least 27% share of renewable energy consumption, and (iii) at least 27% energy saving compared with business-as-usual scenario [9, 10]. These policies frameworks are applied in order to develop low-carbon economy and meet EU long-term targets till 2050, which assume, among others, the reduction of GHG emissions by 80-95% as compared to 1900 levels [11].

3.2 Solutions for the reduction of CO₂ emissions

The generally accepted solution for reducing CO₂ emissions into the atmosphere involves the implementation of three strategies [12]: (1) a reduction in energy consumption, (2) a change in what we consume, or (3) a change of our attitude towards the resources and waste. Currently, the most developed strategies are (1) and (2). These two strategies are resulting in lower carbon consumption by development of technologies with higher efficiency, the decrease in consumption of energy per capita and replacement of fossil fuel-based energy sources by renewables, such as wind, solar, biomass etc. However, there is a huge potential in changing our attitude towards greatly produced waste – carbon dioxide. The implementation of carbon dioxide utilization processes is a key element to sustainable development, as strategies (1) and (2) have a limited capacity, and, as it is predicted, fossil fuels will still be our main source of energy in coming decades. The reduction of carbon dioxide can be realized either by carbon capture and storage (CCS) technologies or via utilization of carbon dioxide as a chemical feedstock – CCU (Carbon Capture and Utilization). These two approaches are complementary, and while CCS technologies are aiming at capturing and subsequently storing huge quantities of carbon dioxide, the chemical utilization of CO_2 aims at generating added-value products. Moreover, most technologies, which are currently developed as future CO₂ utilization processes, require pure streams of CO₂. Thus, implementation of both solutions CCS and chemical utilization of CO₂ is required.

3.2.1 CO₂ Capture Systems

Carbon dioxide capture is already, or will be, applied to large scale stationary sources of emissions, such as fossil fuel power plants, fuel processing plants and other industrial installations

(iron and steel, cement and bulk chemicals production). The capture of CO₂ from small and mobile sources (transportation, residential and commercial building sectors) would be rather difficult and more expensive than from large stationary sources, and thus currently capture systems from large scale sources are mainly developed. CO₂ capture systems from installations combusting fossil fuels and biomass include the following types of capture (Fig. 3.2) [12]: (i) post-combustion, (ii) precombustion, (iii) oxyfuel combustion, and (iv) capture from industrial process streams.



Fig. 3.2 Carbon dioxide capture systems from stationary sources (adapted from [12])

In the post-combustion capture systems, the fossil fuel or biomass is combusted in air. Flue gases are passed through a separation equipment which captures CO₂, and the remaining flue gas is discharged to atmosphere. The post-combustion capture system can be applied in fossil fuelfired power plants.

A pre-combustion capture system involves a reaction of a fuel in oxygen or air, and/or steam, in order to obtain synthesis gas (mixture of H₂ and CO) as the main product. Resulting carbon monoxide is further reacted with steam in water gas shift reaction (WGS) to produce H₂ and CO₂ [13]. CO₂ is subsequently separated. In this way a hydrogen-rich fuel is obtained which can be used in many applications, e.g. gas turbines, engines, fuel cells, boilers or furnaces. IGCC plants (Integrated Gasification Combined Cycle) use syngas as a fuel and can apply pre-combustion capture system.

Oxyfuel combustion system assumes the combustion of fuel in the stream of pure oxygen instead of air. In this way, the produced flue gas consists mainly of CO_2 and H_2O . One of the drawbacks of this system is high temperature of flames, which is a result of combustion of fuel in pure oxygen [13]. However, a part of flue gases (H_2O and CO_2) can be recycled to the reactor in

order to moderate combustion temperature. The second drawback is associated with high costs of oxygen separation from air.

The capture of CO₂ from industrial processes can apply similar techniques as postcombustion, pre-combustion and oxyfuel combustion systems. This could be applied to such processes as purification of natural gas, production of hydrogen-rich synthesis gas for manufacture of ammonia, alcohols, liquid fuels, cement and steel production and fermentation processes for food and drink production [13].

3.2.1.1 CO₂ separation technologies

The methods of CO₂ separation from flue gases, which are mainly applied in postcombustion capture system, as well as in capture from industrial processes, are based on physical and chemical processes, such as absorption, adsorption, membranes, cryogenic separation and chemical reactions (chemical looping) [13].

Chemical absorption process typically use amines e.g. MEA (Monoethanolamine). The stream of flue gases is bubbled through MEA solution, resulting in the formation of MEA carbamate. CO₂ and MEA are regenerated by heating. The technique has some drawbacks, as it is highly energy intensive, has a low CO₂ loading capacity and MEA is degraded by other components of flue gasses such as SO₂, NO₂, HCl, O₂. Instead of MEA, other amines can be used e.g. diethanolamnie (DEA), methyldiethanolamine (MDEA), or other materials such as activated carbons. The absorption with aqueous ammonia solution is possible, if other flue gases components were oxidized (SO₂ to SO₃, NO to NO₂), which results in less energy demanding process (40% reduction) [12]. Physical absorption techniques use in e.g. dimethyl ethers of poly(ethylene glycol).

Adsorption techniques usually apply solid materials, such as activated carbons, molecular sieves, polymers, templated silicas, materials with strong affinity for CO₂ and with good adsorption/desorption capacity. Adsorption/desorption cycles are carried out by the change of pressure (PSA - pressure swing adsorption) or temperature (TPA – temperature swing adsorption). This processes are generally considered low energy intensive and cost effective [12], but its drawback is high amounts of adsorbent necessary connected with high volumes of flue gases in stationary power plants.

Other separation technique applies membranes which allow the penetration of a specific gas through them. The driving force in the membrane method is a difference in pressure, thus this technique can be applied for high pressure flue gases. The materials such as polymers, metals or ceramics found application as membranes in industrial processes to separate H₂ from flue gases,

 CO_2 or O_2 . The membrane techniques has not yet been applied for CO_2 capture on a large scale, due to the problems with reliability and low cost required for CO_2 capture [13].

Cryogenic distillation, which is e.g. applied for O₂ separation from air, can be also used to separate CO₂ from flue gases. The process requires condensation of gas to liquid by a series of compression, cooling and expansion steps, and subsequent distillation [13]. The drawback of this method is its high cost and high energy intensity. However, a high purity stream of CO₂ can be obtained.

CLC (Chemical Looping Combustion) technologies can be also applied for CO_2 separation [12]. They are relatively new methods which are currently being developed. CLC processes require the application of metal oxides in e.g. NiO, CuO, Fe₂O₃ or Mn₂O₃ (oxygen carrier). The metal oxide is circulating between two reactors containing air and fuel, respectively. In the air reactor the carrier is oxidized and undergoes subsequent reduction in the fuel reactor, resulting in fuel oxidation and production of H₂O and CO₂. The stream of flue gases containing water and CO₂ is then dehydrated and compressed.

3.2.2 Applications of CO₂

The captured CO_2 can find and finds applications in many areas of industry. The current and potential applications of carbon dioxide are depicted in Fig. 3.3 [14].



Fig. 3.3 The scheme of carbon dioxide applications (adapted from [14])

The current applications of CO_2 involve: food processing, preservation, packing, beverage carbonation, coffee decaffeination, horticulture, fire suppression, urea production, pharmaceuticals production and enhanced oil recovery (EOR). Unfortunately, some of these applications are small scale and carbon dioxide is usually emitted to atmosphere after use, which results in no permanent reduction of CO_2 emissions. The potential future applications involve biological and chemical conversion of CO_2 , which can result in long-term CO_2 fixation and thus real reduction in CO_2 emissions.

The application of carbon dioxide as chemical feedstock for fuels and chemicals production will be discussed in more details in the next subchapter.

3.2.2.1 General application of CO₂

The current technological uses of CO₂ are minor and low-volume. It is estimated that only around 15-20 Mt/year is utilised in this way and most probably this value will not increase significantly in the coming decades [12].

CO₂ is applied in food production to carbonate soft drinks, beers and wine. Most of CO₂ used in carbonization of beverages is obtained in the fermentation process. Since CO₂ has a contact with food it has to be of high purity, thus application of purified CO₂ streams from other sources in e.g. fertilizers production is also possible. Other application in food production is packing under controlled atmosphere, which reduces microbial growth in the processed food and limits food oxidation [12]. Supercritical CO₂ is also used for decaffeination of coffee on industrial scale [15] or to extract flavours and fragrances.

Carbon dioxide is also used in fire suppression either in fire extinguishing systems, or is injected into materials in order to decrease their flammability. Another current small scale application is to use CO_2 as a refrigerant in vapour compression systems [12]. Frozen solid CO_2 (dry ice) is also applied for refrigeration of foodstuffs, meat products and other frozen foods. Dry ice has also found application in many technical processes where low temperature is required.

Water treatment plants use CO₂ for remineralization of desalted and highly soft waters produced by desalination plants. Iron and steel industries, textile and dying industries, power plants and paper industry produce alkaline wastewater, which must be neutralized before it can be discharged. CO₂ can be used to change pH of these waste waters as an alternative to mineral acid naturalization [16].

3.2.2.2 Enhanced Fossil Fuel Recovery

Enhanced fuel recovery techniques can be applied to store CO₂ in the extracted fields of oil, natural gas or coal. The method involves injection of CO₂ into a depleted fossil fuel field, which acts as a solvent that reduces in e.g. viscosity of oil, enabling it to flow to the production well. While the production is complete, CO₂ can be permanently stored in the field. This method allows to increase oil and natural gas production, and is considered to be relatively safe.

Enhanced Coal Bed Methane Recovery (ECBM) is a process similar to EOR and EGR. In this process, CO₂ is injected into a deep depleted coal field in order to enhance the recovery of methane, which can be then used for electricity production or exported to market. While EOR and EGR are mature technologies, applied mainly in the United States, the ECBM is currently developed.

Enhanced fuel recovery technologies have high potential of CO_2 storage. The U.S. Department of Energy estimated that till 2010 in US around 0.56 Gt CO_2 had been consumed by CO_2 EOR, and total CO_2 storage capacity in US for oil and gas reservoirs had been equal to ca. 138 Gt CO_2 [17]. On the other hand, enhanced fossil fuel recovery processes increased production of fossil fuels, and thus the overall CO_2 reduction effect can be smaller.

3.2.2.3 Biological use of CO₂

Biological uses of CO_2 are focused on application of carbon dioxide in man-made active photosynthesis systems (eq. 3.1), for production of food biomass and biofuels. Although large-scale biological technologies of CO_2 have not yet been implemented, their potential has been confirmed on laboratory and pilot-scale [12, 18, 19].

$$6 \text{ CO}_2 + 6 \text{ H}_2\text{O} + \text{sunlight} \Rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2$$
(3.1)

Carbon dioxide can find application in horticulture, where it is provided to greenhouses in order to maintain optimal concentration of CO₂ and maximize plant-growth. Another important application of CO₂ is to use it to stimulate marine organisms growth in. e.g. algae, which are a rich source of biomass. Both production systems can be used either as a source of biomass, which can undergo combustion or gasification to produce energy, or algae organisms can be a source of triglycerides for the production of biofuels. The concept of producing energy in large-scale industrial biofarms can be realized in 'algal biorefineries' [19].

The potential of application of CO_2 for biological uses is very high. It has been estimated that 1.8 tons of CO_2 is required for the production of 1 ton of algal biomass [19]. Moreover, these technologies involve high-volume low-quality CO_2 and therefore it is possible to use flue gases from power plants.

3.3 Utilization of CO₂ as a chemical feedstock

The image of carbon dioxide on the scientific, societal and industrial levels has drastically changed during the last few decades. Carbon dioxide is no longer considered a harmful pollutant, but a valuable chemical and an important carbon source. The CO₂ capture and separation technologies, which are currently applied or are under development, can provide high purity CO₂ streams for the production of chemicals and fuels. There are already existing large-volume technological processes (refineries, ammonia production, ethylene oxide production, gas processing, H₂ production, liquefied natural gas, biorefineries), which can be treated as a source of pure CO₂ available for CCU technologies [20]. As mentioned in the previous subchapter, CO₂ already finds a number of applications. However, its use as chemical feedstock has still a huge potential with a number of industrial opportunities and advantages [21, 22]:

- CO₂ becomes an interesting raw material with almost zero or even negative costs.
- CCU technologies can create a positive public image of companies, as with the increasing political and social pressure on reducing CO₂ emissions, carbon dioxide will be utilized to valuable products.
- Instead of inactive storage of carbon dioxide (CCS), CO₂ will be recycled. It will also reduce the costs of CO₂ transport.
- With the production of new chemicals companies can gain new market shares.
- CCU gives opportunities to produce organic chemicals in a safer way, as many organic synthesis produce pollutants as e.g. CO₂ is 'green' alternative for toxic phosgene in organic synthesis of polycarbonates.



Fig. 3.4 Catalytic routes for CO₂ transformation into fuels and chemicals (adapted from [23])

Fig. 3.4 presents current and potential technologies which use CO₂ for the production of synthetic fuels and added-value chemicals. It is predicted that processes involving CO₂ conversion will be developed on industrial scale in the coming decades, creating in this way a new carbon dioxide based economy [23]. Since all of these reactions require the presence of catalysts, this clearly points to the importance of catalytic studies of these chemical reactions on laboratory and pilot scale.

CO₂ conversion to fuels, rather than organic chemicals, is expected to play a major role in CO₂ emission management strategies. Firstly, because fuels market is much larger than the market of organic chemicals. Secondly, CO₂ emissions are mainly associated with the production of energy from fossil fuels. As reported by Centi et al. [21] around 5-10% of current total CO₂ emissions is suitable for the production of fuels, which corresponds to reduction of ca. 1.75-3.5 Gt CO₂ emissions per year. As the processes of CO₂ conversion into fuels are energy demanding, there is a need to apply and develop renewable technologies in order to supply energy for these chemical reactions. Thus, carbon dioxide and CCU technologies are a key element of our sustainable development.

Table 3.1 summarizes different routes for chemical CO₂ utilization, taking into account six criteria, which influence the implementation of CO₂ utilization technologies on industrial scale, together with their advantages and drawbacks. The study was performed by Thybaud and Lebain for the French Environment and Energy Management Agency [24]. Table 3.1 allows to overview a degree of development of the existing and future technologies. The criteria which were used to analyse different CO₂ valorisation routes were [20, 24]:

- Potential development: it indicates the time required to open the first industrial facility, which depends mainly on research and development efforts.
- Economic prospective: it indicates the prospects of achieving an economic return and reflects the difficulty to remove economic blocks that currently exist.
- External use of energy: it indicates the cost of energy consumption per cost of the product. The energy consumption is a major issue and therefore can strongly limit possible industrial application of technology. This concerns mainly endothermic processes, such as dry methane reforming.
- Potential volume of use of CO₂: it indicates maximum annual amount of CO₂ which could be potentially used by year 2050.
- Time of sequestration: it represents CO₂ fixation time before it is released to the atmosphere, and
Other environmental impacts: they indicate the application of toxic chemicals in the process, environmentally dangerous catalysts etc.

		Potential development	Economic perspectives	External use of energy	Potential vol. of CO ₂	Time of sequestration	Other impacts on environment
_	EOR	4	4	3	2	4	4
Already Idustria	Industrial use	4	4	3	2	1.5	4
A ine	Organic synthesis	4	3	2	3	3	3
τε	Hydrogenation	3	3	2	4	2	3
Sho terr	Algae open ponds	3	3	4	4	2	4
lium rm	Reforming of hydrocarbons	2	Not known	1	4	2	1
Mec te	Algae reactor	2	2	4	4	2	4
	Mineralization	1	1	1	3	4	3
	Thermo chemical	1	2	4	4	2	3
Long term	Electrolysis	1	Not known	2	4	2	2
	Photo Electro Catalysis	1	Not known	4	4	2	2
	Bio catalysis	1	Not known	4	4	2	3

Table 3.1 Summary of the different options in the valorisation of CO₂ (adapted from [20]

Potential development: 1, more than 10 years \rightarrow 4, industrial

Economic perspectives: 1, difficult to estimate \rightarrow 4, available industrial data

External use of energy: 1, difficult to decrease \rightarrow 4, no need

Potential vol. of CO₂: 1, less than 10 Mt \rightarrow 4, more than 500 Mt

Time of sequestration: 1, very short \rightarrow 4, long term

Other impacts on environment: 1, significant \rightarrow 4, low (solvents or toxic chemicals, metal resources)

In the following part of the chapter, the selected CCU technologies were presented. The electrocatalytic, electrolysis and bio-catalytic routes were not taken into account. Although these technologies are currently widely researched, they still require deep studies, as their efficiencies

and degrees of conversion are still too low in order to consider commercialization. The review of selected technologies for the chemical utilization of CO₂ clearly shows that the reduction of CO₂ emissions is not limited to CCS technologies and CCU is a key element to mitigate CO₂.

3.3.1 Physicochemical properties of carbon dioxide – CO₂ activation

Carbon dioxide is a gas at normal temperature and pressure. At normal pressure and temperature below $-78.5^{\circ}CCO_2$ becomes solid (dry ice). CO_2 may be turned to liquid by compressing it to the corresponding liquefaction pressure and removing produced heat at temperatures between triple point temperature and critical temperature. CO_2 is in a supercritical state (sc- CO_2), where it behaves as a gas, at temperatures higher than 31.1°C and pressures higher than 73.9 bar. Physical and chemical properties of CO_2 are summarized in Table 3.2.

CO ₂	Critical temperature	31.1°C
44.0059 g/mol	Critical pressure	73.9 bar
C(27.29%) O(72.71 %)	Critical density	467 kg/m ³
44.7 cm ³	Triple point temperature	-56.5°C
16	Triple point pressure	5.18 bar
1.16 Å	Boiling point (1.013 bar)	-78.5°C
180°	Solubility in water at STP	1.716 vol/vol
13.73 eV	Gas density at STP	1.976 kg/m ³
3.8 eV	Gas specific volume at STP	0.506 m ³ /kg
	CO ₂ 44.0059 g/mol C(27.29%) O(72.71 %) 44.7 cm ³ 16 1.16 Å 180° 13.73 eV 3.8 eV	CO2Critical temperature44.0059 g/molCritical pressureC(27.29%) O(72.71%)Critical density44.7 cm³Triple point temperature16Triple point pressure1.16 ÅBoiling point (1.013 bar)180°Solubility in water at STP13.73 eVGas density at STP3.8 eVGas specific volume at STP

 Table 3.2 Physical and chemical properties of carbon dioxide [25-27]

CO₂ is a linear 16e⁻ molecule which contains two polar C=O bonds, although the whole molecule is non-polar with two sets of orthogonal π orbitals. Two bonds between C and O atoms have a distance of 1.16 Å. CO₂ has a ionization potential of 13.73 eV and an electron affinity of 3.8 eV, and thus it is a poor electron donor and good electron acceptor. Carbon dioxide is a very stable molecule and thus its activation requires high energy inputs and highly active metal catalysts, usually transition metals. Two different reaction sites are present in carbon dioxide molecule. Carbon atom, of Lewis acid character, is an electrophilic centre, and oxygen atom, of weak basic Lewis character, is a nucleophilic centre. Most catalytic reactions require activation of both acidic and basic centres, so that carbon and oxygen atoms can interact with metal catalysts. Moreover, the π electrons in 2 C=O bonds can also interact with d electrons of transition metals. The activation of carbon dioxide involves acceptance of electron in CO₂ π orbital which causes bending of a molecule (the OCO angle close to 133° [28]), resulting in the change of the molecular energy and the increase of bond length between carbon and oxygen atom. Carbon dioxide is the lowest in energy of all carbon-containing binary neutral species. It is also, together with water, the end product of any combustion process of organic compounds, and therefore is lying in a potential energy well, as illustrated in Table 3.3 [28]. In general the reactions in which CO₂ reacts with OH⁻ ions, amines or olefins (CO₂ is built into organic molecule and C atom does not change its oxidation state) are examples of exothermic processes that do not require energy input. Therefore, the appropriate catalyst could convert CO₂ to useful organic chemicals, such as carboxylates and lactones (RCOOR'), carbamates (RR'NCOOR''), ureas (RR'NCONRR'), isocynates (RNCO) or carbonates [(ROC(O)OR'], creating in this way an alternative for more polluting processes currently in use [28]. On the other hand, reactions in which a reduced form of CO₂ is obtained as a product are endothermic processes, and thus require the input of energy in the form of heat, electrons or other radiation. By applying these processes, it is possible to obtain formates (HCOO-), oxalates [C(O)O]₂²⁻, formaldehyde (H₂CO), carbon monoxide (CO), methanol (CH₃OH), dimethyl ether (CH₃OCH₃) and methane (CH₄) [28].

Compound	State	ΔH⁰ (kJ/mol)	ΔG⁰ (kJ/mol)	ΔSº (J/K)
CO	g	-110.5	-137.2	827.7
<u>(</u> 0-	aq	-413.3	-	-
	g	-393.51	-394.4	895.1
CO ₃ ²⁻	aq	-675.2	-	-
CaCO ₃	S	-1100	-	-
CH_4	g	-74.4	-50.3	780.0
C_2H_4	g	52.5	68.4	919.4
OCH ₂ CH ₂ OC(O) ethane carbonate	S	-586.3	-	-
	I	-277.7	-174.8	672.8
C2H5OH	g	-235.1	-168.5	1183.6
	S	-455.3	-	683.3
	g	-387.5	-	1271.9
C ₆ H ₆	I.	49.0	-	-
C ₆ H₅COOH	S	-385.2	-	701.7
HOC ₂ H ₄ COOH	S	-589.9	-	-

Table 3.3 The energy of formation of chemicals relevant to CO₂ (adapted from [28])

3.3.2 Urea synthesis

Urea is produced from carbon dioxide and ammonia (eq. 3.2).

$$CO_2 + 2NH_3 \rightleftharpoons H_2NCOONH_4 \rightleftharpoons CO(NH_2)_2 + H_2O$$
(3.2)

The industrial process requires high temperatures and pressures. The facilities to produce urea are often placed close to ammonia plants, as large quantities of CO_2 are separated during the production of hydrogen via steam reforming and WGS reaction to produce synthetic gas.

The urea production is currently one of the most important technologies in which carbon dioxide is chemically utilized. In 2011 with the production of ca. 153 million tonnes of urea, around 112 million tonnes of carbon dioxide were consumed. On the other hand, urea is most commonly used as an agricultural fertilizers, and thus the fixation time of used CO₂ is relatively short, as it is released again into atmosphere after application [29].

3.3.3 Synthesis of salicylic acid

The production of salicylic acid is carried out via Kolbe-Schmitt method. CO₂ is reacting with sodium phenolate at high pressures and temperatures (eq. 3.3). Salicylic acid and its derivatives found applications as pharmaceuticals, food preservatives etc. [30]. Typically the CO₂ fixation time is short-term, as it is released rapidly after application.



On the other hand, there is a possibility of application of salicylic acid as a monomer for the production of polycarbonates and polyesters, which could increase CO₂ fixation period [29].

3.3.4 Synthesis of carbonates, cyclic carbonates and polycarbonates

Carbonates and cyclic carbonates are important organic compounds applied as solvents, intermediate reactants in organic synthesis and monomers. The current production of these chemicals involves the reaction of appropriate alcohols with toxic phosgene. An alternative route is to react CO₂ with alcohols (eq. 3.4) or epoxides (eq. 3.5), to obtain respectively carbonates and cyclic carbonates [30].

The recent trend in organic synthesis is to use ionic liquids as solvents and catalysts. CO₂ possesses the ability of dissolving in ionic liquid phase. Therefore synthesis of cyclic carbonates from CO₂ and epoxides can be performed with the application of ionic liquids. It has been reported, that they act as a catalysts in cyclic carbonates formation, resulting in the increase in selectivity and beneficial effect on the reaction rate [31].

There is also a possibility to obtain polycarbonates in this way (eq. 3.6) [29]. Polycarbonates are a class of thermoplastic polymers, which can transmit light. They are also used as pore-forming agents in ceramic industry [30]. This class of polymers can also find application in polyurethane production. Thus, there is an opportunity to use CO₂ as large-scale polycarbonate systems. The very important advantage of such processes is long-term fixation of CO₂ for decades or even years [29].





There are a few examples of commercialization of the production of polycarbonates in e.g.: BASF initiative for the production of polypropylene carbonate or Asahi Kasei's process leading to aromatic polycarbonates (phosgene-free synthesis) [20].

3.3.5 Production of inorganic substances – mineralization

A large scale storage option for CO_2 is its mineralization in geologic formation. The processes are based on the reaction of carbon dioxide with metal oxides, such as MgO, CaO etc., to form inorganic carbonates (eq. 3.7).

$$CO_2 + M^{\parallel}O \rightleftharpoons M^{\parallel}CO_3 \tag{3.7}$$

CO₂ can be fixed by the reaction with natural silicate minerals, rocks containing alkalineearth oxides or waste materials from industry such as fly-ashes or metallurgic slags [30]. Carbonation process can be performed underground as a method of storage of CO₂, or as an industrial process. In this way CO₂ can be used for the production of calcite (CaCO₃), which is applied in industry as a polymer filling material, raw material for optical glasses or pharmaceutical preparations [29]. There is also a possibility of obtaining hydrotalcite-like materials in a reaction of CO₂ with magnesium oxide and sodium aluminate. This class of layered materials has a wide range of applications in industry and catalysis and will be discussed in Chapter 5.

Mineralization of CO_2 not only gives additional value products for industry, but also has a long time of CO_2 fixation and can help to utilize other industry waste products together with CO_2 .

3.3.6 CO₂ – gasification of coal

The technology of coal gasification has been known for many decades and was applied on industrial scale as early as 1800s for the production of heating and light. With the development of natural gas and oil technologies the development of the process paused. History has shown that the technology is revisited when access to oil, natural gas and petroleum products is limited due to high prices or scarcity. Today gasification technology has again gained much attention and is being strongly developed. The process involves coal conversion into suitable fuel gas by the reaction with gasification agents such as air, steam, CO₂ or their mixtures, giving as a product a mixture of carbon monoxide, hydrogen, methane and carbon dioxide. The main reactions during gasification process are [32]:

$$C + O_2 \rightleftharpoons CO_2 \tag{3.8}$$

$$C + \frac{1}{2}O_2 \rightleftharpoons CO \tag{3.9}$$

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2 \tag{3.10}$$

$$C + H_2 O \rightleftharpoons H_2 + CO \tag{3.11}$$

$$C + CO_2 \rightleftharpoons 2CO \tag{3.12}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3.13}$$

$$C + 2H_2 \rightleftharpoons CH_4 \tag{3.14}$$

The coal gasification is a complex process consisting of coal pyrolysis and exothermic partial combustion (eq. 3.8-3.10), the latter providing heat for the endothermic gasification (eq. 3.11, 3.12). The process itself can be accompanied by WGS reaction (eq. 3.13) and due to the presence of ash, methane formation can be catalysed (eq. 3.14). The gasification technology could contribute to the reduction of CO_2 emissions by using carbon dioxide as a gasification agent. Additionally, the application of CO_2 in gasification mixture can increase process efficiency and reduce coal and oxygen consumption. The pilot plants which apply this technology are currently being developed [33].

3.3.7 CO₂ – Oxidative Dehydrogenation (ODH)

 CO_2 can be used as an oxidative agent in oxidative dehydrogenation process for converting paraffins to valuable olefins. The classic dehydrogenation process (eq. 3.15) is equilibrium limited, highly endothermic and thus requires high inputs of energy. The oxidative dehydrogenation process (eq. 3.16) uses oxygen, making process exothermic. The application of CO_2 in ODH (eq. 3.17) which is a mild oxidant, not only decreases demand for energy, but also favours selectivity to olefins [23]. Moreover, CO_2 is less expensive and less aggressive oxidant than O_2 .



The intensive studies are carried out to find an appropriate catalyst for CO₂ ODH reaction. One of the important processes of ODH in the presence of CO₂ is dehydrogenation of ethylbenzene to styrene, an important monomer in petrochemical industry. In general, catalysts with redox properties, such as ceria-zirconia, have been reported as efficient materials for styrene production [23]. CO₂ can play several roles in ODH process, depending on the used catalyst and reaction. It can participate in redox cycle by producing oxygen species and reoxidize reduced oxides. It can also oxidize carbon deposits formed during ODH process.

3.3.8. Production of synthesis gas

The mixture of hydrogen and carbon monoxide, known also as synthesis gas or syngas, is a very important industrial gas used for the production of many chemicals (Fig. 3.5) [34].

In 2010 syngas production was over 70 000 MW_{th}, 45% of which was used to produce chemicals and 38% to produce liquid fuels [20]. Synthesis gas is currently produced on industrial scale via steam reforming of methane (eq. 3.18) on nickel-based catalysts, or gasification and pyrolysis of carbonaceous materials (See Chapter 3.3.5). However, very interesting alternative is to produce synthesis gas from methane in dry reforming process (DRM) (eq. 3.20), which will be discussed in more details in the next chapter. Another alternative is to perform partial oxidation of methane (POM) (eq. 3.19). The reforming routes for production of synthesis gas are summarized in Table 3.4.



Fig. 3.5 Applications of synthesis gas in chemical industry (adapted from [34])

Table 3.4 Methane	reforming	processes	resulting ir	n synthesis	gas
		p. 0000000			0~~

Main reaction	∆H ₂₉₈ ⁰ (kJ/mol)	Equation
$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	206	(3.18)
$CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2$	-36	(3.19)
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	247	(3.20)
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	247	(3.21)
$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	206	(3.22)
In excess of methane, heat from CH ₄ combustion:		Equation (3.18) (3.19) (3.20) (3.21) (3.22) (3.22) (3.23) (3.23) (3.24) (3.25) (3.26) (3.27) (3.28)
$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$	-880	(3.23)
Combination of SRM, DRM and POM		
mpanying and side reactions:		
$H_2O + CO \rightleftharpoons CO_2 + H_2$	-41	(3.24)
$H_2 + CO_2 \rightleftharpoons H_2O + CO$	41	(3.25)
$2CO \rightleftharpoons C + CO_2$	-172	(3.26)
CH₄ ≓C + 2H₂	75	(3.27)
$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$	-802	(3.28)
	Main reaction $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ $CH_4 + 1/2O_2 \rightleftharpoons CO + 2H_2$ $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ In excess of methane, heat from CH_4 combustion: $CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$ Combination of SRM, DRM and POMmpanying and side reactions: $H_2O + CO \rightleftharpoons CO_2 + H_2$ $H_2 + CO_2 \rightleftharpoons H_2O + CO$ $2CO \rightleftharpoons C + CO_2$ $CH_4 \rightleftharpoons C + 2H_2$ $CH_4 \rightleftharpoons C + 2H_2$ $CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$	Main reaction ΔH_{298}^{0} (kJ/mol) $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ 206 $CH_4 + V_2O_2 \rightleftharpoons CO + 2H_2$ -36 $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ 247 $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ 247 $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ 247 $CH_4 + H_2O \rightleftharpoons CO + 3H_2$ 206In excess of methane, heat from CH_4 combustion:206 $CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$ -880Combination of SRM, DRM and POM-880 $M_2O + CO \rightleftharpoons CO_2 + H_2$ -41 $H_2O + CO \rightleftharpoons CO_2 + H_2$ -41 $H_2 + CO_2 \rightleftharpoons H_2O + CO$ 41 $2CO \rightleftharpoons C + CO_2$ -172 $CH_4 \rightleftharpoons C + 2H_2$ 75 $CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$ -802

In the view of chemical CO₂ utilization, DRM reaction is the most interesting one. However, due to the deactivation of catalysts via formation of coke and sintering of active material, combinations of reforming reactions are applied: (i) combination of SRM and DRM to reduce formation of catalytic coke by oxidation of carbon deposits via WGS reaction in the presence of water, (ii) autothermal reforming, i.e. the combination of exothermic POM and endothermic reforming process (DRM or SRM), in order to modify H₂/CO molar ratio and decrease amount of energy required to power the reforming reaction, (iii) tri-reforming of methane (TRM), with the combination of SRM, DRM and POM reactions [30].

Tri-reforming process may directly produce synthesis gas with a desired H₂/CO molar ratio by modification of feed gas composition, i.e. $H_2O/CO_2/O_2/CH_4$ ratios. The process is especially interesting, as it could directly use flue gas from a power station, without the necessity of energyintensive and expensive CO₂ separation stage [35, 36]. Since in the flue gases from power stations O_2 and H_2O are present, the TRM process is affected also by WGS reaction and methane oxidation, which makes TRM a very complex chemical process.

3.3.9 Hydrogenation of CO₂

Hydrogenation of carbon dioxide is currently undergoing large development. This technology has the greatest potential to be developed on a large scale in the nearest future [20]. The hydrogenation process covers a large number of catalytic reactions, such as production of methanol, dimethyl ether, methane, formic acid and higher alcohols and hydrocarbons. The common element for all these processes is the need for a cheap and CO₂-emission-free source of hydrogen. In general, this requires the application of renewable energies to power electrolysis of water (see Chapter 3.3.7.1). Another common issue is that products obtained via hydrogenation of CO₂ are produced currently through conversion of H₂/CO mixture. Thus, it is believed that the first stage of CO₂ hydrogenation process is in fact RWGS reaction (eq. 3.25) resulting in H₂ and CO mixture, and subsequently the formation of desired products. The type of product obtained in hydrogenation process is dependent on the type of used catalysts. Therefore, hydrogenation of CO₂ requires very selective catalysts in order to avoid undesired by-products.

3.3.9.1. Methanol production from CO₂

Methanol is the most important product of synthesis gas conversion with approximate annual usage of 65 million tonnes in 2013 [20]. The current technology uses synthesis gas obtained from fossil fuels (3.29). The reaction is mainly catalysed by Cu/ZnO-based catalysts. The new method of MeOH production, which could help CO_2 mitigation is to use a CO_2/H_2 mixture (eq. 3.30).

$$CO + 2H_2 \approx CH_3OH; \ \Delta H_{298K}^0 = -90.8 \text{ kJ/mol}$$
 (3.29)

$$CO_2 + 3H_2 \Rightarrow CH_3OH + H_2O; \Delta H_{298K}^0 = -49.8 \text{ kJ/mol}$$
 (3.30)

Though methanol synthesis has a huge potential as one of the CCU technologies, it should be stressed that the source of hydrogen for the process is a very important issue. Peters et. al [29] analysed different hydrogen sources in the CO_2/H_2 methanol production taking into account: (1) conventional methanol synthesis with H₂ production via steam reforming of natural gas, (2) methanol synthesis from CO_2/H_2 mixture with H₂ obtained from natural gas, (3) H₂ from the electrolysis of water, whereby the electricity was produced in the 2011 German power plant mix, and (4) H₂ from electrolysis of water using hydroelectric power. Only in the latter case, the implementation of methanol production from CO_2/H_2 mixture resulted in the net decrease of CO_2 emissions (Table 3.5).

Scenario of H ₂ production	CO ₂ emissions associated with H ₂ and MeOH production (t_{CO2}/t_{CH3OH})	CO ₂ fixed (t)	CO ₂ released (t)
(1)	0.24	-	+0.24
(2)	1.91	1.38	+0.53
(3)	5.67	1.38	+4.29
(4)	-	1.38	-1.38

Table 3.5 CO₂ emissions associated with methanol synthesis (adapted from [29])

Methanol finds applications in the various areas of industry. The worldwide demand was estimated at 30 million tonnes in 2011 [29]. Methanol and its derivatives can be widely used in the fuel sector of economy, as a fuel itself or its derivatives, e.g. dimethyl ether (DME). The methyl tetrbutyl ether (MTBE), which is obtained from MeOH conversion, is used as an anti-knocking additive for combustion engine fuels. Fatty Acid Methyl Ethers (FAMEs), used as biodiesel, are obtained in transesterification of fats with methanol. Moreover, the methanol-to-gasoline (MTG) process is another option to obtain synthetic fuels from methanol. Thus, the CO₂ based synthesis of methanol could address the needs of petrochemical industry and transportation sector.

The fixation of CO₂ into fuels via methanol production and its derivatives is not a longterm solution, as CO₂ is released during combustion process. However, it can be treated as one of the methods of energy transport and storage. The possibility of a long-term CO₂-fixation is connected to the production of formaldehyde via oxidation of methanol, which can be further converted into aminoplasts or thermoplasts via polymerization. Another, long-term solution is the methanol-to-olefins process (MTO) in which the starting chemicals for polymerization process – alkenes – are obtained [29].

The commercialized plant of methanol synthesis from CO₂/H₂ mixture are already in use, in e.g. Carbon Recycling International plant in Iceland [37] or Mitsui Chemicals plant in Singapore.

It is generally expected that the market of methanol production from CO₂ will rapidly grow in the coming years [20].

3.3.9.2 DME production

Dimethyl ether had gained much attention in recent decades, because of its various applications. DME is used in organic synthesis and as an aerosol propellant, but most importantly this chemical can be a diesel substitute, and thus DME is considered as a fuel of XXI century [38]. The conventional production of DME is carried out via methanol dehydration (eq. 3.31) or by synthesis gas conversion (eq. 3.32). Indirect methanol dehydration for production of DME requires the presence of acid catalysts (intermediate strength), while direct production from synthesis gas involves the application of bifunctional catalysts, usually Cu on solid acid catalyst.

$$2CH_3OH \Rightarrow CH_3OCH_3 + H_2O \tag{3.31}$$

$$2\text{CO} + 4\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \tag{3.32}$$

$$2CO_2 + 6H_2 \Rightarrow CH_3OCH_3 + 3H_2O$$
 (3.33)

An alternative way for DME production is to apply a CO_2/H_2 mixture (eq. 3.33). Similarly as in methanol production this method may help to mitigate CO_2 . However, the source of H_2 used in the process is an important issue. The reaction proceeds also on bifunctional Cu-based catalysts [23].

3.3.9.3 Methanation – production of CH₄

Sabatier reaction (eq. 3.34) i.e. hydrogenation of CO_2 to produce methane is a very promising process, which has already been applied in small-scale pilot plants [39, 40].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{3.34}$$

The research in this area is mainly concentrated in Germany in e.g. Audi e-gas process for production of CH₄ for automotive use [20]. In the past, the methanation technologies were used mainly for purification purposes, in e.g. to remove CO in ammonia synthesis plants or in refineries to obtain pure stream of H₂. Nowadays, the application of methanation technology has changed course and the process is considered as a method of fuel production and as a method of energy storage for excess of electrical energy from renewable sources [39].

Methanation is a highly exothermic reaction, which is usually carried out at temperatures between 200-500°C in the presence of Ni- or noble metal-based catalyst [23]. Currently, the

research on this process is focused on developing active and stable catalysts, but also on the process design (reactor design, process parameters etc.).

3.3.9.4 Production of formic acid

Formic acid is an important industrial chemical with a number of applications. The current method of HCOOH production involves conversion of synthesis gas (c.p. Fig. 3.5). Use of formic acid in fuel cells as a suitable hydrogen storage material is considered one of the most important future application. HCOOH is decomposed to CO₂ and H₂ without the formation of carbon monoxide. CO₂ produced in the process could be recycled to HCOOH via its hydrogenation. However, the direct synthesis of formic acid from H₂ and CO₂ mixture is thermodynamically unfavourable (eq. 3.35, ΔG^0 =32.9 kJ/mol). Even the implementation of high CO₂/H₂ pressures leads to low equilibrium conversions. Thus, synthesis in homogeneous phase was proposed, which involves the application of a base, which shifts equilibrium and results in the formation of HCOO⁻ (eq. 3.36). The method involves application of Rh, Ru and Ir organometallic complexes as catalysts [23].

$$CO_2 + H_2 \rightleftharpoons HCOOH$$
 (3.35)

$$CO_2 + H_2 + NH_3 \rightleftharpoons HCOO^2 + NH_4^+$$
(3.36)

3.3.9.5 Hydrocarbons synthesis

The Fischer-Tropsch (FT) synthesis in a conventional way synthesises hydrocarbons (HC) from syngas. In the view of CO_2 utilization, the CO_2/H_2 mixture could be also used for the production of HC in FT-like synthesis. The path to higher hydrocarbons involves either methanol synthesis and subsequent hydrocarbons formation (eq. 3.37), or RWGS reaction and subsequent FT synthesis (eq. 3.38) [23].

 $H_2 \longrightarrow -CH_2 - + H_2O$ (3.37)

$$CO_2 H_2$$
 CH₃OH + H₂O ---- gasoline (3.38)

The studied catalytic systems for these process are based on conventional FT catalysts, mostly on Co and Fe. The Co-based catalytic systems with CO₂/H₂ mixture yields high selectivities to methane. The low selectivity towards higher hydrocarbons can be explained by low activity of Co catalyst in RWGS reaction. On the other hand, high selectivity to higher hydrocarbons was observed for Fe-based catalytic systems [41].

4 Dry Reforming of Methane

Worldwide natural gas consumption increases. In 2014 world natural gas consumption was equal to 12.9 Gtoe, which was 22.5% higher with the respect to year 2004. Only to the last year an increase of 0.9% in natural gas consumption was observed [42]. This trend is predicted to develop even faster as natural gas is the cheapest fossil fuel and possesses the highest H/C ratio, which contributes to lower CO₂ emissions with respect to other fossil fuels [43]. At the same time CO₂ emissions connected with the consumption of natural gas were equal to ca. 6.9 Gt in 2013, which accounted for ca. 22% of total CO₂ emissions [5]. Whence, natural gas and carbon dioxide are closely connected. Finding an appropriate solution to ease an environmental impact of these two gases is crucial for sustainable development towards low-carbon economy and can be realized via dry reforming of methane process.

The first investigations concerning converting CO_2 and CH_4 into synthesis gas were reported in 1888. The process was further investigated by Fischer and Tropsch in 1928 [44]. Thus DRM process is not a new concept. Nowadays, dry reforming reaction has again gained much attention due to the possibility of utilizing two greenhouse gases (carbon dioxide and methane) and the production of a very valuable mixture of H_2 and CO - a building block for the production of liquid fuels and chemicals. Moreover, DRM can utilize natural gas fields which contain high amounts of CO_2 and are currently economically unprofitable to be extracted. Such gas fields often contain, apart from hydrocarbons, also carbon dioxide, whose concentration can vary from a few percent up to even 70%, as reported e.g. for Natuna natural gas field in Indonesia [45]. Studies carried out by Suhartanto et al. [45] confirmed possible application of DRM technology for this field, which, as confirmed, contains ca. 1302 billion cubic meters of gaseous hydrocarbons.

4.1 Comparison of DRM with respect to other reforming processes

Synthesis gas can be produced from methane through different routes such as steam reforming of methane (SRM), DRM, partial methane oxidation (POM), autothermal reforming or trireforming process (Chapter 3.3.8, Table 3.4). The obtained H₂/CO molar ratio varies depending on the type of oxidant applied in a given process. The commercialization of DRM would be beneficial not only from the environmental perspective, but also because DRM could become a good alternative for other syngas producing reactions.

Steam reforming has been developed on the industrial scale in 1930s, and since then was strongly developed, becoming nowadays the main technology of syngas production which operates at or near its theoretical limits [46, 47]. SRM process gives the highest H₂/CO molar ratio around 3,

making it a suitable method for hydrogen production via water gas shift WGS. In this way e.g. H_2 for ammonia synthesis plants is produced. However, WGS reaction produces high amounts of CO₂. On the other hand, such high H_2 /CO molar ratio makes syngas from SRM unsuitable for other chemical process, such as synthesis of organic oxygenated compounds (methanol, acetic acid) or hydrocarbons. In Fischer-Tropsch (FT) synthesis high H_2 /CO ratios limit carbon chain growth [46]. In this way DRM reaction, which gives H_2 /CO molar ratio around unity, can be considered more suitable for FT synthesis for production of long chain hydrocarbons or valuable oxygenated chemicals.

SRM and DRM reactions are both endothermic and thus require high energy inputs, which are currently supplied for SRM process by the combustion of fossil fuels, contributing in this way to the growth of CO₂ emissions [48]. The generally accepted solution, in order to contribute to CO₂ emissions reduction, is to power DRM process by either renewables or nuclear energy. Moreover, SRM process is considered rather expensive, as it operates at high pressures (higher than DRM [49]) and requires high-temperature steam, which generates additional costs. Er-rbib et al. [49] compared SRM and DRM processes in terms of energy balance and CO₂ emissions for the production of synthesis gas and further H₂ production via WGS reaction (Table 4.1). Their studies clearly show, that DRM can contribute to reduction of CO₂ emissions while producing synthesis gas. On the other hand, DRM is rather not suitable for H₂ production, as production of 1kg of H₂ via DRM requires ca. 1.5 times more energy than SRM. At the same time application of DRM is connected to lower or negative CO₂ emissions with respect to SRM for both syngas and H₂ production. Although both processes give synthesis gas, the composition of the obtained product differs. Thus SRM and DRM can be used to supply syngas for different chemical processes and markets.

	Steam reforming	of Methane (SRM)	Dry reforming of Methane (DRN			
	Energy balance	CO ₂ balance	Energy balance	CO ₂ balance		
Synthesis gas production	6.65 MJ/kg(CO+3H ₂)	0.45 kgCO ₂ /kg(CO+3H ₂)	4.35 MJ/kg(2CO+2H ₂)	-0.44 kg CO ₂ /kg(2CO+2H ₂)		
Hydrogen	27 MI/kgHa	7 kaCO-/kaH-	42.7 MI/kgHa	2.34 kgCO-/kgH-		
production	MJ/kgH ₂	$kgCO_2/kgH_2$	MJ/kgH ₂	kgCO ₂ /kgH ₂		

Table 4.1 Energy and CO₂ balances of steam and dry reforming of methane processes (adapted from [49])

Syngas can be also produced via partial methane oxidation, which was first investigated in the 1930's and 1940's [46]. POM is an exothermic process, and thus does not require such high energy inputs as SRM and DRM. On the other hand, the process requires pure stream of O₂, which generates additional costs. The performance of POM process in the stream of air, is considered not beneficial due to the high content of balance N₂. Moreover, high exothermicity of the reaction can generate additional problems, such as hot spots in catalysts, and thus make process control difficult. At the same time, it is very important to control POM, as CH₄ and O₂ can form an explosive mixture [46]. The process gives H₂/CO molar ratio around 2, making it suitable for the market competition with DRM.

In order to eliminate high energy demand for SRM and DRM reactions, the concept of autothermal reforming (ATR) was developed. ATR technology is a combination of POM and SRM, or POM and DRM, so it includes both exothermic and endothermic reactions. The energy released in POM is consumed by the endothermic reaction, making the process autothermal. The feed gas composition influences the obtained H₂/CO molar ratio. Typically, the values of H₂/CO between 1 and 2 are obtained. The main drawback of ATR process is high cost of oxygen separation [50].

Tri-reforming (TRM) process seems to be the most advantageous method of syngas production. The combination of SRM, DRM and POM makes the process suitable for direct conversion of flue gases from fossil fuelled power plants to synthesis gas. Typically, flue gas from fossil fuelled power plant contains 12-14% CO₂, 8-10% H₂O, 3-5% O₂ and 72-77% N₂, while that form natural-gas fired one contains 8-10% CO₂, 18-20% H₂O, 2-3% O₂ and 67-72% N₂ [51-53]. However, there is still a problem of high concentration of balance N₂. This issue can be resolved by implementation of oxyfuel combustion, which results in the decrease of N₂ concentration of flue gases. Depending on the applied conditions, such as temperature and feed gas composition, it is possible to tailor thermal effect of the process to obtain mildly endothermic, almost thermoneutral or mildly exothermic process, and an appropriate distribution of the obtained products (H₂/CO molar ratio) [36]. It must be stressed, however, that TRM process, due to the presence of a large number of reagents, is influenced by the occurrence of a large number of side reactions, which makes the chemistry of the process hard to study.

4.2 Thermodynamics of the DRM

As mentioned in Chapter 4.1, dry reforming of methane is highly endothermic reaction and high temperatures are required in order to obtain considerable conversions of CH_4 and CO_2 . Additionally, there is a number of possible side reactions which may occur during DRM process, and thus thermodynamic analysis of the process is important. Partial information concerning thermodynamic equilibrium calculations studied based on the minimization of Gibbs free energy is available in literature [54-61]. Nikoo et al. [54] studied the thermodynamics of DRM reaction in the view of carbon formation. Istadi et al. [55] investigated the possibilities of the formation of C_2 hydrocarbons, but the possible C-forming reactions were not analysed. Li et al. [56] compared thermodynamic calculations for autothermal, steam and dry reforming processes. The analysis of DRM at high pressures was performed by Chien et al. [57]. Shamsi et al. [58] reported thermodynamic data of two carbon-forming reactions in DRM process: CH₄ decomposition and Boudouard reaction. Sun et al. [59] analysed the thermodynamics of steam and dry reforming in a view of their solar thermal applications. Soria et al. [60] and Ozkara-Aydinoglu [61] carried out the thermodynamic analysis of combined SRM-DRM systems. Propane dry reforming was analysed by Wang et al. [62].

4.2.1 Thermodynamics of side reactions

Table 4.2 presents the list of possible reactions which may occur in DRM process. The reactions (or group of reactions) are [43, 54, 55, 58, 59, 61]:

- Reverse water gas shift RWGS (eq. 4.2) accompanies DRM reaction in whole temperature range
- Carbon forming reactions (eq. 4.3-4.6):
 - \Box CH₄ decomposition (eq. 4.3.) favoured at high temperatures;
 - □ Boudouard reaction (eq. 4.4) favoured below 550°C;
 - Hydrogenation of CO and CO₂ (eq. 4.5-4.6) do not influence process significantly;
- Oxidative coupling reactions (eq. 4.7-4.8) occur at high temperatures;
- Dehydrogenation (eq. 4.9) occurs at high temperatures;
- Hydrogenation of CO and CO₂ (eq. 4.10-4.12) at high temperatures favourable towards reverse side
- Methanation (eq. 4.13-4.14) favourable at temperatures below 550°C
- Dehydration (eq. 4.15) highly influenced by equilibrium limitations;
- Reforming reactions (4.16-4.22) tent to occur at high temperatures.

The influence of each reaction presented in Table 4.2 on the overall DRM process is different. In general, as the main side reactions are considered RWGS (eq. 4.2), CH₄ decomposition (eq. 4.3) and disproportionation of CO (eq. 4.4). The influence of other reactions is rather insignificant [54, 55]. However, they still need to be taken into account, as e.g. reforming reactions (eq. 4.16-4.22) can contribute to the syngas production. The temperature ranges in which the main DRM side reactions are favoured are presented in Fig. 4.1.

Reaction number	Reaction	ΔΗ ⁰ ₂₉₈ (kJ/mol)
	Dry reforming	
4.1	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	+247
	Reverse Water Gas Shift	
4.2	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	+41
	Carbon forming reactions	
4.3	$CH_4 \rightleftharpoons C + 2H_2$	74.9
4.4	$2CO \rightleftharpoons C + CO_2$	-172.4
4.5	$CO_2 + 2H_2 \rightleftharpoons C + 2H_2O$	-90
4.6	$CO + H_2 \rightleftharpoons C + H_2O$	-131.3
	Oxidative coupling of methane	
4.7	$2CH_4 + CO_2 \rightleftharpoons C_2H_6 + CO + H_2O$	+106
4.8	$2CH_4 + 2CO_2 \rightleftharpoons C_2H_4 + 2CO + 2H_2O$	+284
	Dehydrogenation	
4.9	$C_2H_6 \rightleftharpoons C_2H_4 + H_2$	+136
	Hydrogenation of CO and CO ₂	
4.10	$CO + 2H_2 \rightleftharpoons CH_3OH$	-90.6
4.11	$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	-49.1
4.12	$CO_2 + H_2 \rightleftharpoons HCOOH$	15
	Methanation	
4.13	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	-165
4.14	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	-206.2
	Dehydration	
4.15	$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$	-37
	Reforming	
4.16	$CH_3OCH_3 + CO_2 \rightleftharpoons 3CO + 3H_2$	+258.4
4.17	$C_2H_6 + 2H_2O \rightleftharpoons 2CO + 5H_2$	+350
4.18	$C_2H_6 + 2CO_2 \rightleftharpoons 4CO + 3H_2$	+430
4.19	$C_2H_4 + 2CO_2 \rightleftharpoons 4CO + 2H_2$	+290
4.20	$C_2H_4 + 2H_2O \rightleftharpoons 2CO + 4H_2$	+210
4.21	$CH_3OCH_3 + 3H_2O \rightleftharpoons 2CO_2 + 6H_2$	+136
4.22	$CH_3OCH_3 + H_2O \rightleftharpoons 2CO + 4H_2$	+204.8

Table 4.2 The main reactions which may occur during dry reforming of methane (adapted and modified from [54])



Fig. 4.1 Temperature ranges in which the main side reactions during DRM process are favourable

4.2.2 Optimal conditions for DRM reaction

Basing on the thermodynamic analysis of DRM process presented in literature [54-62], some general remarks concerning optimal conditions for dry reforming of methane can be formulated:

- Considerable conversions of both CH₄ and CO₂ and H₂/CO molar ratios around unity can be reached at temperatures higher than 700°C and atmospheric pressure. (DRM is thermodynamically favourable above 700°C).
- Carbon formation can be suppressed by introducing the excess of CO₂ into reaction system and carrying out the process at high temperatures.
- The reaction is favourable at low pressures, as at high pressures carbon formation increases and CO₂ and CH₄ conversions decreases.
- Introduction of other oxidizing agents such as water or O₂ can also decrease carbon formation [56, 59-62].

The above remarks are very general. The high temperatures of reaction promote DRM route and inhibit side reactions. However, from the economic and technical perspective it would be more beneficial to perform DRM process at temperatures lower than 700°C. In order to do that, active, stable and selective catalysts needs to be introduced into the DRM reaction system, which

can promote a kinetic inhibition of carbon formation and shift selectivity of the process towards DRM.

4.3. Catalysts for dry reforming of methane

Carbon dioxide is a stable molecule, thus its chemical activation requires highly active metal catalysts, as discussed in Chapter 3.3.1. The catalytic performance of the material may be affected by numerous variables, such as active material, support, promoter, calcination temperature and conditions, reducing environment, preparation method, particle size, shape, and reactor selection.

During last decades great efforts have been undertaken to develop of highly active and stable DRM catalysts. The deactivation of DRM catalysts is mainly caused by: (i) the formation of catalytic coke, which may result in the blockage of pores and active sites, (ii) sintering of active material, as DRM is carried out rather at high temperatures, or (iii) oxidation of metallic active sites. The application of different types of materials, preparation methods and application of promoters may lead to overcoming these problems. The following subchapter discusses the literature information on the influence of these variables on catalytic activity of materials tested in DRM process.

4.3.1 The role of active component

It has been reported that in general transition metals of 8, 9 and 10 groups of periodic table (VIII group metals in old classification) are active materials for DRM reaction i.e. iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum (Fig. 4.2). There are no reports regarding Os-based catalyst. Table 4.3 lists different sequences of catalytic activity in DRM reaction reported for these transition metals. Moreover, it is important to stress, that the selection of active phase in catalysts affects, besides activity, also catalyst selectivity and stability, which can be more critical properties where commercialization of catalytic process is concerned.

Solymosi et al. [63] investigated the catalytic activity of noble metals supported on alumina (Pt, Pd, Rh, Ru, Ir), which, in terms of turnover numbers, followed the sequence: Ru>Pd>Rh>Pt>Ir. This sequence was the same as the ability of noble metals to dissociate CO_2 . The largest amount of coke deposits was observed for Rh and Pt catalysts and the least for Pd-containing one. The authors found that methane alone showed little reactivity towards supported noble metals. Their conclusion was that activity of noble metals in DRM reaction was associated with their ability to dissociate CO_2 to adsorbed CO and O species, which in turn, can promote dissociation of methane to adsorbed CH_x and H species, and thus DRM reaction. Ashcroft et al. [64] compared activity of noble metals with non-noble nickel supported on alumina. The highest activity towards DRM was observed for Ir- and Rh-based catalysts, which did not exhibit the formation of coke deposits during 200h tests, and showed conversions of CH₄ and CO₂ equal to almost 90% at 777°C. The high conversions of CH₄ and CO₂ over Ni/Al₂O₃ catalyst (higher than for Pd and Ru) were observed due to the higher loading of active phase. However, Ni-based catalyst showed the highest amount of coke deposits after catalytic tests. Similar effect was observed by Barama et al. [65] and Hou et al. [66].

1 IA 1A		Periodic Table of the Elements										18 VIIIA 8A					
1 *1 Hydrogen 1.008	2 IIA 2A		Nob	le met	als			Atomic Number	Valence Charge			13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	² He Helium 4.003
3 +1 Lithium 6.941	4 *2 Be Berytlium 9.012		Non	noble	transi	tion m	netals	Syr Na	mbol ame			5 *3 B Boron 10.811	6 Carbon	7 N Nitrogen 14.007	8 2 Oxygen 15.990	9 1 F Fluorine 18.908	10 Neon 20,180
11 *1 Na Sodium 22.000	12 *2 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 	10	11 IB 1B	12 IIB 2B	13 *3 Aluminum 26.982	14 *4 Silicon 28.086	15 +5,+3,-3 Phosphorus 30,974	16 +6.2 Sulfur 32.000	17 1 Chlorine 35.453	18 ° Argon 30.948
19 *1 K Potassium 38.008	20 *2 Ca calcium 40.078	21 *3 Sc Scandium 44.958	22 ** Ti Titanium 47.88	23 V Vanadium 50.942	24 +6.+3.+2 Cr Chromium 51.996	25 +7.+4.+2 Mn Manganese 54.938	26 +3.+2 Fe Iron 56.033	27 +3.+2 Co Cobalt 58,933	28 ⁺² Nickel 58.000	29 +2,+1 Cu Copper 63.546	30 *2 Zn _{Zinc} 65.39	31 *3 Gallium 69.732	32 *4 Ge Germanium 72.81	33 +5,+3 As Arsenic 74,922	34 4.2 Se Selenium 78.972	35 *3.1 Br Bromine 79.904	36 Kr Krypton 84.80
37 *1 Rb Rubidium 84.468	38 +2 Sr Strontium 87.62	39 +3 Yttrium 88.906	40 ** Zr ^{Zirconium} 91.224	41 *5 Nobium 92.906	42 +6.+4 Mo Molybdenum 95.95	43 TC Technetium 68.007	44 +4.+3 Ruthenium 101.07	45 *3 Rh Rhodium 162.906	46 +4.+2 Pd Palladium 100.42	47 *1 Ag Silver 107.868	48 *2 Cd Cadmium 112411	49 *3 In Indium 114,818	50 +2.4 Sn Tin 118.71	51 +3 Sb Antimony 121.760	52 Tellurium 127.6	53 +51 lodine 126.904	54 ° Xenon 131.29
55 *1 Cs Cesium 132.005	56 *2 Ba Barium 137,327	57-71	72 *4 Hafnium 178.49	73 *5 Ta Tantalum 180.948	74 +6,+4 W Tungsten 183.85	75 +5.+4.+3 Re Rhenium 186.207	76 *4 Os ^{0smium} 190.23	77 +L+3 Ir Iridium 110.22	78 +4.+2 Platinum 195.08	79 +3 Au Gold 198.967	80 *2.+1 Hg Mercury 200.59	81 *3.+1 TI Thailium 204.383	82 *2 Pb Lead 207.2	83 *3 Bi Bismuth 208.980	84 *4 Polonium [208.982]	85 -1 At Astatine 209.987	86 ° Rn Radon 222.018
87 *1 Francium 223.020	88 *2 Radium 225.025	89-103	104 *4 Rf Rutherfordium	105 unk Db Dubnium [262]	106 unk Sg Seaborgium [265]	107 unk Bh Bohrium (284)	108 unk Hassium (269)	109 unk Mt Meitnerium [268]	110 unk DS Darmstadtium [299]	111 unk Rg Roentgenium [272]	112 unk Copernicium [277]	113 unk Uut Ununtrium unknown	114 unk Fl Flerovium [289]	115 unk Uup Ununpentium unknown	116 unk Lv Livermorium [298]	117 unk Ununseptium unknown	118 unk Uuuo Ununoctium unknown
	Lantha Seri	nide es	*3 58 anum 006 Cer 140	•a 59 • • • • • • • • • • • • • • • • • • •	** 60 1 dymium 208 ** 144	d ⁺³ 61 P Prom 24 14	*3 ethium 1,913	*3 63 E arium 0.36 15	Eu ⁺³ 64 Gade 11,965	*3 65 T Tert 150	-b bium 18 1925 - 18	rosium 2.50 *3 67 H Holr 184	+3 68 68 Erb 1930	Er ⁺³ 69 T Thum 7.26 16	m tilum 170 Ytter 177	*3 71 Lute 3.04 *3 71 Lute 174	+3 .tium 1967
	Actin Seri	ide es Actin 227/	C 190 Ium 128	rium .038 91 Protac 231	* 92 a Urar 238	J ium 029 93 N 93 N 93 N 23	" 94 P unium 7,048 94 Piute 244	95 Pu onium 1.054	100 micium 3.061 96 Cu Cu 24	rium 7.070 97 Berk 241	selium 7.070 *** 98 Calife 251	ornium 1.080 ¹ 99 Einste 12	100 S F Finium 541	101 Mende 25	elevium 88.1	elium A 101	ncium 62)

Fig. 4.2 The metals which showed catalytic activity in dry reforming reaction

CO₂ reforming of methane over Pt, Rh, Rd, Ir, Pd and Ni supported magnesia catalysts was examined by Rostrup-Nielsen et al. [67]. The catalytic performance of prepared materials was compared in SRM and DRM reaction. The obtained results showed that Rh- and Ru-based catalysts were the most active ones in DRM reaction, with high reaction rates and no carbon deposition. A similar catalytic activity was registered by Ni, Pt and Pd catalysts. However, Ni-based catalysts exhibited high amounts of carbon whiskers-like deposits. The authors showed that passivation of Ni-based catalyst by sulphur could enhanced its resistance to coke formation, but in order to obtain high reaction rates higher temperatures than those for Rh- and Ru-based catalysts were required.

Tsyganok et al. [68] proposed an efficient method of introducing precious metals (Ru, Rh, Ir, Pt, Pd, Au) into the structure of hydrotalcite-derived Mg(Al)O mixed-oxides. Ru or Rh containing catalysts showed the highest conversions of CH_4 and CO_2 . Over these two catalysts conversions of CO_2 were a few percent higher than those of CH_4 , pointing to the occurrence of RWGS. The highest catalytic activity and resistance to coke formation was observed for Ru-based catalyst which was

additionally tested over 50h timer on stream (TOS). The good performance was ascribed to high dispersion of very small (under 1.5 nm) Ru crystallites on the catalyst surface. Pt-containing catalyst showed much lower activity and the activity of Pd catalyst was suppressed by heavy formation of coke deposits. Au turned out to be practically inactive in DRM.

The performance in DRM reaction of Fe, Co and Ni supported on ceria was compared by Asami et al. [69]. The highest activity at 850°C was observed for Ni/CeO₂ catalysts. As over 20h on stream, no change in CO₂ and CH₄ conversions, as well as H₂/CO molar ratios close to unity were observed. It was stated that Ni/CeO₂ catalyst did not undergo deactivation. This was ascribed to strong metal-support interactions. However, at 700°C deactivation of Ni/CeO₂ catalyst was observed. Co-based catalyst also showed good conversion of CH₄ and CO₂. However, the initial values of CH₄ conversion were low, due to incomplete reduction of cobalt species. Fe/CeO₂ catalyst had the lowest activity and poor selectivity, caused by the deactivation of catalyst.

The theoretical calculations considering activity in DRM on (111) planes of transition metal surfaces (Cu, Ni, Pd, Pt, Rh, Ru, Ir and Fe) were performed by Hei et al. [70]. The authors studied heats of chemisorption, activation barriers and enthalpy changes for different species involved in DRM reaction on transition metal surfaces, and based on obtained results proposed the mechanisms of DRM reaction, which will be discussed in Chapter 4.4, and the activity sequence: Fe > Ni > Rh > Ru > Ir > Pd > Pt > Cu. Authors stated that noble metals could desorb CO before its decomposition to carbon, while Fe and Ni tended to dissociate CO to carbon and oxygen. Thus nonnoble metals catalysts promoted carbon forming reactions, which affected their stability.

It must be mentioned, however, that the direct comparison of activity of transition metals in DRM reaction as reported in literature [63-69, 71, 72], is rather difficult as the reported catalysts (Table 4.3) were tested under different reaction conditions (temperature, contact time, feed gas composition), as well as different supports were used, which may influence metal-support interactions. Thus only general conclusions may be withdrawn. The noble metal-based catalysts show good activity and selectivity in DRM reaction. Among noble metals, Rh- and Ru-based catalysts are the most active ones [63, 65-67, 70], but the better chances of industrial applications the latter, as ruthenium is cheaper than rhodium [70].

Active material	Support or carrier	Reaction conditions	Activity Sequence	Ref.
1 wt.% Pd, Rh, Ir, Ru, 2 wt.% Pt; IMP	Al ₂ O ₃	Temp. 500°C m _{cat} = 300mg; CH ₄ /CO ₂ =1/1; GHSV = 3000-6000h ⁻¹ Reduction: 1h at 500°C	Ru > Pd > Rh > Pt > Ir	[63]
1wt.% Pd, Ru, Rh, Ir, Ni*; IMP	Al2O3	Temp. 777°C; m _{cat} =50mg; CH ₄ /CO ₂ =1/1; GHSV=40000h ⁻¹	lr > Rh > Ni > Pd > Ru	[64, 71, 72]
0.9-1.4 wt% Ni, Ru, Rh, Pd, Ir, Pt 16 wt.% Ni; IMP	MgO-Al ₂ O ₃ alumina-stabilized magnesia, MgAl ₂ O4	Temp. 500, 650°C; m _{cat} = 10-50mg; CH ₄ /CO ₂ /H ₂ =4/16/1.6	Ru > 16 wt.% Ni/MgAl ₂ O₄ > Rh ≈ Ni > Ir > Pt > Pd	≈ [67]
Rh, Ru, Pt, Pd, Ir (5 wt.%); Ni, Co (10 wt.%); IMP	α-Al ₂ O ₃ mesoporous Al ₂ O ₃	Temp. 800°C; CH ₄ /CO ₂ =1/1; GHSV=60000 or 120000 cm ³ /g _{cat} h; Reduction: 800°C for 1h;	Ni > Rh > Ru > Co > Ir > Pt > Pd	[99]
3, 5 and 10 wt.% Ni, Rh, Pd, Ce; IMP	Al-pillared montmorillonites	Temp. 650°C; CH4/CO2/He=1/1/8; mcat=500mg; flow 12 dcm ³ /h;	3% Rh ≈ 10%Ni >>Pd >> 3%Ni >> Ce	[65]
2 wt.% Ru, Rh, Ir, Pt, Pd, Au,	Hydrotalcite-derived Mg(Al)O mixed-oxides	Temp. 800°C CH₄/CO₂/N₂=23/23/35; Flow/Weight = 92727 cm³/g _{cat} h	Ru ≈ Rh > Ir > Pt >> Pd >> Au	[68]
5 wt.% Fe, Co, Ni; IMP	CeO ₂	Temp. 700°C; CH₄/CO₂/Ar=1/1/3 Reduction: in H₂/Ar (2/3 vol/vol) at 700°C for 1h	Ni > Co >> Fe	[69]

Table 4.3 The influence of the type of metal on catalysts activity in DRM. Catalytic tests carried out in fixed-bed reactor at atmospheric pressure.

From non-noble metals, only nickel-based catalysts showed similar activities and selectivities to those reported for noble metals. Activity of nickel-based catalyst may be enhanced by introduction of higher loadings of active phase than noble metals [65-67]. On the other hand, non-noble metals show tendency to promote carbon-forming reactions which can cause catalyst deactivation and reactor plugging. In general high resistance of noble metals to coke formation can be explained by the fact that that they do not dissolve carbon to such high extent as in e.g. Ni, which is responsible for the formation of carbon deposits, in the latter case.

Noble metals are usually introduced onto catalyst support in small amounts, due to their high price, and thus form small crystallites which promotes carbon-free operation [73, 74].

Despite better performance of noble-metal-based catalysts, most of the reported research is focused nowadays on nickel-based ones, as Ni is much cheaper and more available [74]. In comparison to other non-noble metals, e.g. Fe, Co, nickel-based catalysts are less prone to coking [70]. This is why, the next part of this chapter will be focused on nickel-based catalysts tested in dry reforming of methane.

4.3.2 Nickel-based catalysts

Nickel was found to be the most suitable non-noble catalyst in DRM reaction. The research on nickel-based catalyst is currently focused mainly on increasing catalysts stability. The high endothermicity of dry reforming of methane requires high reaction temperatures. This unavoidably leads to the sintering of nickel particles, as its Tammann temperature is equal to 600°C [75]. Moreover, it also accelerates the deactivation via carbon deposition, as carbon-forming reactions proceed more easily on large nickel crystallites [73]. Therefore, several approaches have been proposed in order to increase stability of Ni-based catalysts, such as [76]:

- Employing appropriate catalysts preparation method to inhibit coke growth.
- Using metal oxides with strong Lewis basicity as supports or promoters, as basic sites enhance CO₂ adsorption. Metal oxides can promote oxidation of carbon deposits (reverse Boudouard reaction), but, on the other hand, supports which exhibit Lewis acidity enhance formation of coke deposits.
- The addition of second metal, i.e. noble metal, which can enhance the transport of hydrogen and/or oxygen between active site and support by spillover, and can influence the mechanism of coke formation.
- Sulphur passivation of Ni catalysts, which blocks the step edge sites where coke build-up is initiated.

Changing reaction conditions by the addition of oxidizing agents, such as water or oxygen which can help to oxidize carbon deposits.

In this subchapter an overview of the research for Ni-based catalyst carried out during ca last 20 years is presented. More general reviews of catalysts for dry methane reforming were discussed by Edwards and Maitra [77], Wang and Lu [78], Bradford and Vannice [44], Hu and Ruckenstein [73], Fan et al. [79], Lavoie [43] and recently by Usman et al. [80].

4.3.2.1 The role of support

The role of support in the catalyst is very important. It determines the dispersion of catalytically active metal particles and resistance to sintering, stabilizes and promotes active sites, provides large active surface area, may participate in the reaction itself and can modify catalytic properties of active phase and thus in e.g. increase resistance to coking [47, 74]. In DRM reaction, nickel-based catalysts on various supports were tested, such as single oxides (Al₂O₃ [81-87], MgO [88-93], CeO₂ [94-96], ZrO₂ [97], SiO₂ [75, 98, 99], ordered mesoporous silica – SBA-15 [100], La₂O₃ [101], TiO₂ [102]), mixed oxides (MgO-Al₂O₃ [103-106], CeO₂-ZrO₂ [107, 108], CeO₂-Al₂O₃ [109]), zeolites (zeolite Y, zeolite A, zeolite X, ZSM-5) [110], clays (clinoptolite [111], diatomite [112], vermiculite [113], montmorlonite [114]) and carbon-based materials (carbon nanotubes, activated carbon) [115] (Table 4.4).

Ni				Reaction conditions					Н./СО	
(wt. %)	Support	PM ¹⁾	Temp. (°C)	CH₄/ CO₂	GHSV (h ⁻¹)	TOS (h)	CH₄ (%)	CO₂ (%)	H2/CO (-)	Ref.
10.3	γ -Al ₂ O ₃	IMP	800	1/1	nd	6	92	94	0.98	[81]
ca. 10	Al₂O₃ aerogel	SG	700	1/1 ²⁾	nd	30	55	62	nd	[82]
10	γ -Al ₂ O ₃	IMP				4-5	66	68	nd	
13	γ -Al ₂ O ₃	IMP	750	1/2	3000	nd	94	83	0.81	[83]
5	AI_2O_3	IMP	700	1/1	nd	24	64	70	nd	[87]
10	MgO	IMP	650	1/1	36000	10	63	75	0.85	[88]
10	MgO	СР	700	1/1	14000	5	67	77	0.87	[91]
1	14.0		650	a (a ²)	1	12	23	nd	0.5	[00]
nd	MgO	IMP	800	1/12	nd	12	66	nd	0.9	[89]
10	MgO	SG/E	750	1/1	30000	25	54	69	1.12	[92]
10	MgO	IMP	700	2/1	12000	20	45	nd	nd	[93]
15	MgO-	SG	800	1 /12)	26000	40	84	89	nd	[102]
12	AI_2O_3	СР	800	1/1 ′	30000	40	84	89	nd	[102]

 Table 4.4 Catalytic activity of Ni-based catalysts in DRM reaction. Effect of the support.

Ni			R	Conv	ersion					
(wt. %)	Support	PM ¹⁾	Temp. (°C)	CH₄/ CO₂	GHSV (h ⁻¹)	тОS (h)	CH₄ (%)	CO₂ (%)	H₂/CO (-)	Ref.
10	MgO- Al ₂ O ₃	SCH	700	1/1	24000	53	74	84	1	[106]
5	MgO- Al ₂ O ₃	EISA	700	1/1	15000	100	77	79	0.8	[104]
10 ³⁾	CeO ₂	IMP	760	1/12)	13400	100	65	80	0.83	[94]
5	CeO ₂ (NR) CeO ₂ (NP)	IMP	700	1/1	18000	30	63 58	77 70	0.9 0.9	[95]
5	CeO ₂	IMP	700	1/1	38400	12	37	68	0.6	[96]
3	ZrO ₂	IMP	600	2.2/1 ²⁾	nd	2	53	15	0.75	[97]
2	ZrO ₂	IMP	650	1/1 ²⁾	nd	2	22	14	1.1	[116]
10	CeO ₂ -ZrO ₂	IMP	550	1/1 ²⁾	20000	5	38	37	1	[107]
5	CeO_2 - ZrO_2	IMP	700	1/1	30000	24	39	52	0.7	[108]
10	CeO_2 - Al_2O_3	IMP	800	1/12)	90000	25	75	85	0.88	[109]
10	SiO ₂	IMP	700	1/1	36000	30	68	69	nd	[98]
4	SiO ₂	IMP	700	1/1 ²⁾	nd	65	62	76	nd	[75]
31.5	SiO ₂	SG	750	1/12)	48000	25	54	66	0.68	[99]
8	SBA-15	СР	600	1/12)	20000	24	68	89	0.87	[117]
10	TiO ₂		750	1/1	nd	10	33	nd	nd	[102]
10	CeO ₂ -TiO ₂	IIVIF	750	1/1	nu	10	87	nd	nd	[102]
8	Clinoptilo -lite	IMP	700	1/1	nd	6	69	72	0.9	[111]
5	diatomite	TSD	650	1/1	21120	12	31	41	0.76	[112]
12	Vermicu- lite	IMP	750	2.8/14)	19000	24	96	71	1.1	[113]
10	Montmor -illonite	IMP	700	1/12)	30000	-	77	75	nd	[114]
10	CNs AC	IMP	750	1/12)	Nd	8 -	66 50	78 65	0.85 0.85	[115]

Table 4.4 Continuation

¹⁾ PM – Preparation Method: IMP – Impregnation, SG – Sol-Gel, CP – Co-Precipitation, SG/E – one-pot sol-gel/evaporation, EISA – One-pot evaporation induced self-assembly, SCH –Sonochemistry method, TSD – two-solvent deposition method, MIMP – Melt-impregnation;

 $^{2)}\mbox{CH}_4$ and \mbox{CO}_2 were diluted by inert gas

³⁾ mol %

⁴⁾ tests carried out in the presence of oxygen;

nd-no data

Alumina – Al₂O₃

Alumina is one of the most commonly studied supports for nickel catalysts [73, 74]. It is relatively cheap and possesses high specific surface area, basic character and α -Al₂O₃ phase possesses high thermal stability. However, the catalytic properties of Ni/Al₂O₃ catalyst in DRM reaction and its resistance to carbon formation depends on the catalyst structure, composition, calcination conditions and preparation method. Beccera et al. [81] studied the influence of calcination temperature on activity of impregnated Ni/Al₂O₃ catalysts. With increase of calcination temperature higher amounts of NiAl₂O₄ spinel phase were formed, which suppressed catalytic activity at low temperatures (below 700°C). At reaction temperatures higher than 700°C this effect was not so evident, as calcination temperature did not influence the activity of Ni/Al₂O₃ catalyst. At the same time, the formation of spinel phase increased catalyst resistance to coke formation. As explained by Hu et al. [73] this was the result of strengthening of the Ni-O bond in NiAl₂O₄ with respect to NiO crystal, thus increasing the difficulty of Ni²⁺ reduction to Ni⁰, and resulting in the formation of smaller nickel crystallites on the surface. Similar results were reported by Chen and Ren [83]. Bhattacharyya and Chang [84] also reported that NiAl₂O₄ catalysts prepared via coprecipitation exhibited higher activity and much more stable performance than Ni/Al₂O₃ prepared by physically mixing of NiO and α -Al₂O₃ powders.

Kim et al. [82] compared catalytic performance of impregnated Ni/γ-Al₂O₃ and Ni supported on alumina aerogel prepared by sol-gel method. The preparation method influenced morphology and size of metal particles distributed on catalyst surface, and the catalyst prepared via the latter method exhibited very high specific surface area, high porosity and narrow distribution of nickel particle size. In contrast the former, showed larger size of Ni particles distributed irregularly. This affected catalytic performance in DRM reaction. Ni supported on alumina aerogel was stable up to 30h TOS and its activity was comparable to the reference 5wt.%Ru/Al₂O₃ catalyst. On the other hand, nickel-impregnated catalyst lost its catalytic activity during first 4-5h TOS, due to the formation of carbon deposits. According to the authors, the minimal size of nickel crystallites needed for the formation of whisker-type carbon deposits was 7nm, and thus coking was unavoidable for Ni/Al₂O₃ catalyst prepared by impregnation method. Additionally, due to the weak metal-support interactions sintering of active phase occurred during DRM reaction for such catalysts.

A different approach was applied by Baktash et al. [85], who prepared so called 'inverse catalyst'. Aiming at stabilizing the structure and inhibiting sintering of active Ni crystallites, they coated NiO nanopowder with a thin layer (around few nm) of porous alumina via atomic layer

deposition technique. NiO powder covered with alumina layers showed stable CH₄ conversion of ca. 80%. at 800°C up to 12h TOS. However, catalytic activity decreased with the increase of alumina layer thickness. Additionally, alumina coating prevented sintering of active phase and lead to decreased coking with respect to uncoated catalyst.

Magnesia – MgO

Magnesia was another commonly studied support for DRM nickel-based catalysts. The high Lewis basicity of MgO has beneficial effect, as CO₂ adsorption is enhanced on basic supports, therefore accelerating reaction between CO₂ and deposited carbon species. Another advantage of MgO as a support in DRM arises from the possibility of formation of NiO-MgO solid solution at any molar ratio because of similar anion radii (Mg²⁺ 0.065nm, Ni²⁺ 0.072nm [92]) and lattice parameters. This in turn increases metal-support interactions, and thus prevents catalysts deactivation via sintering.

The effect of nickel loading on (111) magnesia nano-sheets supported catalyst prepared via impregnation was studied by Lin et al. [88]. The stability and activity was reported to be closely related to Ni loadings. The catalytic activity in DRM was increasing with Ni loading up to 10wt.% and then decreased with further increase of Ni content to 20wt.%. Stability for the catalyst with loading higher than 50wt.% was poor. Similar results were reported by Zanganeh et al. [90, 91]. In both studies, the best performance was registered for 10wt.%Ni/MgO catalysts, which was attributed to high basicity of the studied materials and the formation of small nickel crystallites, due to the strong metal-support interactions. It must be mentioned, however, that in both studies the most active catalysts still exhibited the presence of carbon deposits after reaction. The catalysts with low nickel loading (2wt.%) showed decrease in CH₄ and CO₂ conversions which was ascribed to sintering of active nickel phase or oxidation of Ni species. At the same time insignificant amount of catalytic coke was present on the catalyst surface after reaction. In terms of catalyst stability and activity Jafarbegloo et al. [92] also stated that the catalyst loaded with 10wt.% Ni on MgO prepared via one-pot sol-gel/evaporation technique exhibited the best performance with respect to catalysts loaded with higher or smaller amount of Ni. The studies presented in ref. [88, 90-92] showed that CO₂ conversion were always higher than CH₄ conversions in tested temperature range, pointing to the occurrence of RWGS reaction, which decreases H₂/CO molar ratio in the products, over Ni/MgO catalyst. However, only in studies carried out by Jafarbegloo et al. [92] the excess of H_2 in the products of the reaction was observed, which clearly indicates that the method of catalyst preparation influences the occurrence of side reaction and thus the distribution of the obtained products.

Alumina-Magnesia

The beneficial effects of magnesia (enhanced chemisorption of CO₂) and alumina (enhanced thermal stability, high specific surface area) can be combined in mixed MgO-Al₂O₃ support. It has been reported that the addition of MgO into Ni/Al₂O₃ catalyst resulted in the increase of basicity [103, 104], specific surface area and total pore volume [103], due to the formation of MgAl₂O₄ spinel phase. The catalytic activity of Ni supported on mixed magnesia alumina depends on the support preparation method, reaction conditions and pretretment of the catalyst. Min et al. [103] compared the performance of the catalyst synthesized via sol-gel and coprecipitation methods. Both catalysts showed high conversions of CH₄ and CO₂ and were stable for to 40h TOS. Although, the catalysts did not differ in activity, the characterization of catalyst after reaction proved the presence of Ni crystallites of larger size for co-precipitated catalyst than for that prepared via sol-gel method clearly pointing to higher deactivation by sintering. Thus, co-precipitated catalyst was less resistant to coke formation. The authors examined also the effect of Mg/Al molar ratio. The catalysts with medium concentrations of MgO exhibited highest activity. On the other hand, the investigation carried out by Alipour et al. [105] and Xu et al. [104] showed that only a small addition of MgO (up to 5 wt.%) to Ni/Al₂O₃ enhanced its stability and activity.

The formation of Mg(Al)O supported-nickel catalyst may be also realized via thermal decomposition of hydrotalcite-like compounds. These types of catalysts were reported to be very active and stable in DRM reaction [118-134] and will be discussed in details in Chapter 5.

Ceria – CeO₂

Ceria is well known for its high oxygen storage capacity associated with electron transformation between Ce^{3+} and Ce^{4+} [94, 107]. Therefore, the application of ceria support in DRM reaction may be beneficial, due to easier removal of carbon deposits via oxidation by oxygen anions. Moreover, nickel can dissolve in fluorite structure of CeO_2 . The Ni-O-Ce bond is stronger than Ni-O bond in NiO crystal, thus leading to increased metal-support interactions of ceria-supported Ni, resulting in the formation of small Ni particles. The solubility of nickel in CeO_2 is limited to 10-12 mol.% due to the structure limitations, and Ni loadings higher than the solubility limit may result in the loss of its coke-resistance properties, as reported by Yu et al. [94]. The other important factor is morphology of ceria support, as different morphologies are characterized by different oxygen mobility and intensity of interactions with active metal particles. Du et al. [95] compared the DRM performance of ceria nanorods (NR) and nanopolyhedra (NP) structures with that of commercial CeO_2 support. Both nanomaterials exhibited enhanced catalytic activity and stability in comparison to commercial CeO_2 . The best catalytic performance was shown by Ni/CeO₂-NR catalyst, which was

attributed to concentration of surface Ce^{3+} species higher than that for Ni/CeO₂-NP catalyst. Ce^{3+} species were associated with the amount of oxygen vacancies and influenced the type of Ni species present on the catalyst surface, pointing to the importance of oxygen mobility.

Ceria-Zirconia

Another tested support for DRM catalysts was ceria-zirconia. The increase in the number of oxygen vacancies in ceria may be realized via introduction of ZrO₂ into its structure [107]. Zirconia stabilizes ceria by the formation of ceria-zirconia solid solution in the whole composition range. Moreover, ceria-zirconia possesses higher basicity, improved textural features and thermal stability with respect to CeO₂ [108]. However, catalytic activity for zirconia supported Ni catalyst [97, 116] was lower than that reported for Ni/alumina. The effect of Ni loading on Ce_{0.62}Zr_{0.38}O₂ was studied by Radlik et al. [107]. The highest conversions of CH₄ and CO₂ and H₂/CO molar ratio close to unity were observed for the catalyst with 10 wt.% Ni loading. However, this sample exhibited the highest weight loss during TG experiment after reaction, suggesting the lowest resistance to coke formation, which was explained by the largest size of Ni particles on the ceria-zirconia surface. Therefore, it may be beneficial to use lower Ni loadings than 10 wt.%.

Kambolis et al. studied ceria-zirconia binary oxides prepared via co-precipitation with different zirconia content. Mixed CeO_2 -Zr O_2 exhibited better performance than CeO_2 and ZrO_2 alone. The catalytic activity and resistance to the formation of carbonaceous deposits increased with zirconia content and was the highest for the sample with 28 mol % of ceria. As explained by authors, in the presence of Zr^{4+} cations ceria lattice undergoes extensive distortion, which results in the increase of both oxygen mobility and anion vacancies on the surface of binary oxide. The latter may be the active sites for the dissociative adsorption of CO_2 molecule and thus with the introduction of ZrO_2 into ceria structure, the number of DRM active sites increases.

Silica – SiO₂

Silica is another material used typically in catalysis as a support. Huang et al. [98] studied the effect of the preparation conditions of silica support on its catalytic activity in DRM reaction at 700°C. Silica supports prepared via sol-gel method exhibited various types of morphologies and texture such as: yielded sphere, shell-like shape and peanut-like shape. The best activity and resistance to coking was registered for shell-type silica structure. This type of silica carrier exhibited the highest dispersion and the lowest size of Ni particles, as Ni crystallite size depended primarily on the pore size of silica support. It must be mentioned, however, that although the shell-like catalyst showed high conversions of CH_4 and CO_2 (Table 4.4), a huge amount of carbon deposits was present on the catalyst surface after reaction, as spent catalyst exhibited around 60% weight loss. The type of carbon deposits formed on the catalyst surface also depended on silica morphology. Similar results were reported by Zhang and Li [99], who studied core-shell type Ni catalyst in DRM reaction. According to their studies, the micro- and mesopores present in amorphous silica and formed upon material calcination, served as channels through which gas molecules diffused and silica shell structure (narrow pores) suppressed carbon filament growth.

The influence of pre-treatment conditions (reduction and calcination conditions) of Ni impregnated silica catalyst was examined by Kroll et al. [75]. Initial activity of catalyst did not depend on the pretreatment conditions but, with the increase in TOS the differences in catalysts performance were visible. The samples calcined and reduced at high temperatures (700-900°C) exhibited significant loss in catalytic activity, while the unpretreated catalyst showed enhanced stability. Based on the obtained results authors proposed that the active phase for DRM reaction is not metallic nickel, but nickel-carbide-like layer formed at particle surface immediately after contact with the reacting mixture, which explained similar initial activity. The subsequent morphological changes of active phase were depended on the pretreatment procedure and thus influenced activity of catalysts and differences between activity of catalysts were observed.

The catalytic activity of nickel supported on ordered mesoporous silica (SBA-15) prepared via impregnation, precipitation and ascorbic acid-assisted precipitation methods was studied by Galvez et al. [117]. The application of ascorbic acid as a reducing agent, resulted in the formation of a catalyst where Ni species were present in the mesopores of SBA-15, and thus enhanced catalyst activity and stability.

Titania – TiO₂

Titania was also reported as a good support for DRM reaction [102], due to its ability to suppress carbon deposition. TiO_x species, which are formed during reduction with H₂ can migrate to nickel particles and create new active site of Ni-O-Ti³⁺. These new active sites formed at the boundary between active phase and support increase metal-support interactions and promote oxidation of the deposited carbon to CO. Ni/TiO₂ was examined in DRM reaction by Bradford et al. [135] and Ni supported on mixed CeO₂-TiO₂ systems by Kim et al. [102]. The latter catalyst exhibited enhanced performance as compared to Ni/CeO₂ and TiO₂, due to its redox characteristics and higher dispersion of nickel species.

Natural clays and zeolites

Zeolites and natural clays which can be considered a 2D zeolite-like relatively cheap materials, were also studied. Their properties, such as acid-basic properties and thermal stability,

can be tailored to some extent by different chemical and physical treatments [114]. Therefore, their application as adsorbents, catalysts or catalysts supports has gained much attention in recent years. Clinoptilolite is most abundant naturally occurring zeolite. The effect of Ni loading on its catalytic properties has been studied by Nimwattanakul et al. [111]. The catalyst with 8 wt.% Ni showed the highest catalytic activity and considerable stability in DRM reaction at 700°C. Jabbour et al. [112] reported that Ni supported on diatomite was a promising cheap catalyst for DRM reaction. However, the presented results showed that catalyst exhibited slight deactivation during 12h tests, and thus authors suggested that application of promoters might increase catalyst stability. The acid treated, expanded and raw vermiculites were examined by Liu et al. [113]. The best catalytic performance, which authors attributed to its interlayer structure, was registered for expanded vermiculite with 12wt.% Ni. It is worth mentioning that the authors carried out catalytic test in the presence of oxygen, and thus the enhanced stability of materials may be explained by in-situ removal of carbon deposits via combustion.

Carbon materials

Catalytic activity of nickel loaded carbon materials, activated carbon (AC) and carbon nanotubes (CNs), in DRM reaction was examined by Ma et al. [115]. Ni/AC catalyst had lower activity than Ni/CNs, which the authors explained by the collapse of activated carbon structure during the reaction. From the two studied NCs-based catalysts, better performance was shown by the sample into which nickel was introduced inside carbon nanotubes when compared to the sample with nickel crystallites present on the outside surfaces of carbon nanotubes. This was explained by differences in electric density difference between interior and exterior surfaces of CNs and the confinement effect of CNs. The introduction of nickel on and into CNs influenced also the type of carbon deposits present after reaction. Amorphous carbon and graphitic carbon were found, respectively, for the former and the latter catalyst.

Comparison of the supports

A direct comparison of the influence of the supports on catalytic performance in DRM reaction is rather hard, because as presented e.g. in Table 4.4 the catalysts were studied under different reaction conditions (temperature, mass of catalyst, GHSV, flow, CH₄/CO₂ molar ratio), were prepared via different methods (impregnation, co-precipitation, sol-gel method) and underwent different pretreatment procedures (calcination conditions, reduction conditions). All these parameters influence size of metallic nickel particles, the interactions of active phase with the support, and thus may have negative or positive effect on catalyst activity and resistance to the

formation of coke. This is why articles describing tests carried out under the same conditions over different supports for Ni-based catalyst in DRM reaction are presented in Table 4.5.

Tomishige et al. [136] studied the effect of preparation methods (impregnation and coprecipitation) on the performance of Ni/MgO and Ni/Al₂O₃ catalysts. The higher activity was registered for the catalyst supported on magnesia. The best catalyst turned out to be coprecipitated Ni/MgO, which showed the highest conversions of methane and carbon dioxide, and no carbon deposition on the catalyst surface after DRM reaction. The resistance to carbon formation followed the same sequence as that for catalytic activity and was related to the surface basicity and nickel particle size.

Kang et al. [137] compared the performance of nickel supported on alumina and mixed magnesia-alumina. The addition of magnesia to alumina had a beneficial effect on the stability of the catalyst. The authors stated that the formation of carbon deposits during DRM reaction caused fluctuations of CH₄ and CO₂ conversions. The addition of magnesia increased catalyst stability and no fluctuation in CH₄ and CO₂ conversions were observed up to 150h TOS. As reported earlier [103], nickel supported on magnesia or alumina alone was very strongly bonded to the support, due to the formation of NiO-MgO solid solution and NiAl₂O₄ spinel phase, respectively, which resulted in lower activity of the catalysts. The addition of appropriate amount of magnesia resulted in the formation of MgAl₂O₄ spinel phase, and thus weakened the interaction between the support and active phase leading to the increase of activity. At the same time, basicity also increased, which improved the resistance to coke formation and thus enhanced catalyst stability.

Khajeh Talkhoncheh and Haghighi [138] compared catalytic performance of Ni supported on Al₂O₃, CeO₂ and clinoptilolite. In the tested temperature range 550-850°C, the best catalytic performance was observed for alumina supported catalyst. The authors attributed that to the highest value of specific surface area, small crystallite size, and good dispersion and particle size distribution of Ni. Ni/clinoptilolite catalysts exhibited slightly higher specific surface area than Ni/CeO₂, fine particle size and possessed the benefits of natural zeolite-like structure and thus showed performance better than ceria supported catalyst and similar to the that of Ni/Al₂O₃ at 850°C. The other advantage of clinoptilolite was that the cost of mining and treatment of this mineral was lower than the cost of the preparation of alumina catalyst. Therefore, the application of clinoptilolite catalyst in DRM reaction could be beneficial from economic point of view. Unfortunately, carbon formation over the tested catalysts was not discussed.

Ni content/ preparation ¹	Support	Reaction conditions	Activity sequence	Ref.
3 mol.%/CP and IMP	Al ₂ O ₃ , MgO	Temp. 850°C, m_{cat} =100mg, CH ₄ /CO ₂ =1/1, W/F=1.2g _{cat} h/mol; Reduction: in H ₂ at 850°C for 0.5h	NiO-MgO(CP) > Ni/MgO (IMP) > NiO- Al ₂ O ₃ (CP)	[136]
10 wt.%/CP- MBSL	Al ₂ O ₃ , MgO-Al ₂ O ₃	Temp. 700-800°C, m _{cat} =100mg CH ₄ /CO ₂ /He=1/1/1,	MgO-Al ₂ O ₃ > Al ₂ O ₃	[137]
nd/ IMP	CeO ₂ , Al ₂ O ₃ , clinoptilolite	Temp. 550-850°C, m_{vat} =100mg, CH ₄ /CO ₂ =1/1, GHSV=24dm ³ /gh Reduction: in H ₂ /N ₂ =1/9 at 700°C for 1h	Al ₂ O ₃ > Clinoptilolite > CeO ₂	[138]
ca. 1.3 wt.% for TiO ₂ ; 8 wt.% for SiO ₂ and AC; 10 wt.% for MgO /IMP, CP ²	MgO, TiO ₂ , SiO ₂ , activated carbon	Temp. 400-550°C, m _{cat} =5-50mg CH ₄ /CO ₂ /He=1/1/1.8, GHSV=10000-2000 h ⁻¹ Reduction: in H ₂ at 500°C for 1h ³	TiO ₂ > activated carbon > SiO ₂ > MgO ⁴	[135, 139]
10 wt.%/IMP	α-Al ₂ O ₃ , γ- Al ₂ O ₃ , CeO ₂ , La ₂ O ₃ , ZrO ₂	Temp. 550°C, m_{cat} =100mg, CH ₄ /CO ₂ =1, W/F=0.55g _{cat} h/mol; Reduction: in H ₂ at 327°C for 2.5h	γ -Al ₂ O ₃ > α - Al ₂ O ₃ > ZrO ₂ > CeO ₂ > La ₂ O ₃	[140]
4 wt.%/IMP	δ,θ-Al ₂ O ₃ , MgAl ₂ O ₄ , SiO ₂ -Al ₂ O ₃ , ZrO ₂ -Al ₂ O ₃	Temp. 650°C, m _{cat} =50mg, CH ₄ /CO ₂ /N ₂ =1/1/3, Reduction: in H ₂ /N ₂ at 550°C for 1h	$MgAl_2O_4 > ZrO_2 - Al_2O_3 \approx \delta, \theta - Al_2O_3 >> SiO_2 - Al_2O_3$	[141]
8 wt.%/IMP	SiO ₂ , MgO, TiO ₂ , ZrO ₂ , Al ₂ O ₃ , MgO Al ₂ O ₃ -MgO	Temp. 750°C, m _{cat} =100mg, CH ₄ /CO ₂ =1/1, Reduction: in H ₂ /N ₂ at 700°C for 1h	Al_2O_3 -MgO > MgO > SiO_2 > $Al_2O_3 > ZrO_2 >>$ TiO_2	[142]
7 wt.%/IMP	zeolite A, zeolite X, zeolite Y, ZSM-5	Temp. 700°C, m_{cat} =200mg CH ₄ /CO ₂ =1/1, GHSV=30000 Reduction: in H ₂ at 600°C for 1h	Zeolite Y ≈ ZSM-5 > zeolite X >> zeolite A	[110]
2 wt.%/IMP	α -Al ₂ O ₃ , ZrO ₂ , α -Al ₂ O ₃ -ZrO ₂	Temp. 600°C, m_{cat} =25mg CH ₄ /CO ₂ /N ₂ =1/1/6 Reduction: in H ₂ from 25 to 1000°C	α -Al ₂ O ₃ -ZrO ₂ > α -Al ₂ O ₃ > ZrO ₂	[116]

Table 4.5 The effect of support on the catalytic activity of different Ni-based catalyst. Catalytic tests carried out in a fixed-bed reactor and at atmospheric pressure.

¹ Methods of preparation: IMP – incipient wetness impregnation; CP – co-precipitation; CP-MBSL – coprecipitation under multi-bubble sonoliminescene conditions

 $^{\rm 2}$ co-precipitation method was used only for Ni/MgO catalyst

³ Ni/MgO catalyst reduced at 850°C for 0.5h

 $^{\rm 4}$ Ni/MgO catalyst was tested at higher temperature than other catalysts

Nickel supported on SiO₂, TiO₂, MgO and activated carbon was investigated by Bradford et al. [135, 139]. The initial activity of tested catalyst expressed as turnover frequency (TOF), followed the sequence: TiO_2 > activated carbon > SiO_2 > MgO. The catalytic activity of tested materials also followed the ability of the catalysts to activate C-H bond cleavage in methane via electron donation to anti-bonding orbitals in methane. However, only Ni/MgO catalyst, although the least active, did not show deactivation up to 44h TOS. For Ni/TiO₂ deactivation was attributed to the formation of TiO_x species which migrated to nickel crystallites and may have caused blockage of DRM active sites. At the same time, the blockage of active sites by carbon deposits and sintering of nickel species were found responsible for the loss of catalytic activity for Ni/TiO₂, Ni/AC and Ni/SiO₂ catalyst. The authors concluded that the type of support strongly influenced the properties of the catalysts in e.g. electron-donating ability, basicity, metal-support interactions, and thus can suppress carbon-forming reactions. The carbon formation resistivity over the tested catalysts followed the sequence: Ni/MgO > Ni/TiO₂ >> Ni/SiO₂. The low amount of carbon deposits formed on MgO and TiO₂ was attributed, among others, to strong metal support interactions. The high amount of whisker-type carbon deposits was observed over Ni/SiO₂ catalyst, with no metal-support interactions. Ni/MgO catalyst formed NiO-MgO solid solution, thus stabilizing surface Ni-Ni bonds and preventing carbon diffusion into nickel particles, which is believed to be the first stage of whisker-type carbon deposits formation. The authors showed that the type of the support influenced the stabilization of different CH_x intermediates formed via dissociative methane adsorption. The reported values of CH_x were equal to CH_{2.7} for Ni/MgO, CH_{2.4} for Ni/Al₂O₃, CH_{1.9} for Ni/TiO₂ and CH₁ for Ni/SiO₂ [143], which follows the sequence of the catalyst resistance to coke formation.

The catalytic activity of Ni supported on alumina and alumina mixed with MgO, ZrO₂ and SiO₂ prepared via plasma method was investigated by Damyanova et al. [141]. The most beneficial in DRM reaction was the application of MgAl₂O₄ support, which exhibited the highest conversions of CH₄ and CO₂ equal, respectively, to 75 and 81%, as well as values of H₂/CO molar ratio closest to unity. The mixed ZrO₂-Al₂O₃ catalyst showed performance similar to that of the alumina-supported catalyst, while the lowest conversions were observed for SiO₂-Al₂O₃ support. However, only Ni/MgAl₂O₄ catalyst was stable. Catalytic activity followed the same sequence as catalyst resistance to coke formation. The best performance of MgAl₂O₄ catalyst was ascribed to the high number of exposed metal sites, as the catalysts exhibited the smallest Ni particles (ca. 5.1nm) and the highest dispersion. Additionally, according to the H₂-TPR profiles, the applied catalyst reduction conditions were most probably insufficient for the complete reduction of NiO to metallic nickel for these

catalysts. Thus, the coexistence of Ni^{2+} and Ni^{0} species on the catalyst surface might have facilitated the activation of CH_4 and CO_2 , and further enhanced the activity and coke resistance.

Similar observations were reported by Zhang et al. [142], who recently compared catalytic activity of Ni supported on MgO, Al₂O₃, MgO-Al₂O₃, ZrO₂, SiO₂ and TiO₂ in DRM reaction. The highest conversions and stable performance was observed only for Ni supported on a mixed alumina-magnesia catalyst. Ni/SiO₂ catalyst, which exhibited the highest metal dispersion and the highest specific surface area, lost its high initial activity due to the sintering of active phase. The lowest conversions were observed for Ni/TiO₂ catalyst, while other tested samples showed significant decrease in activity with TOS.

Luengnaruemitchai et al. [110] studied different zeolites (zeolite A, zeolite Y, zeolite X, ZSM-5). The tested samples, with the exception of zeolite Y, showed high initial conversions of both methane and CO₂, but the decrease in catalytic activity with TOS was observed. The highest conversions and stable performance was shown by zeolite Y, but at the same time this catalyst exhibited the highest amount of carbon deposits after reaction, though they did not affect the catalytic performance. On the contrary, small increase in CH₄ and CO₂ conversions with TOS was observed, suggesting that carbon deposits formed in the reaction might be not poisonous. However, during the long-term stability tests they may lead to reactor plugging. Interestingly, the obtained values of H₂/CO molar ratios for the zeolite-supported catalysts were higher than 1. When compared to other studies, this clearly indicates that the application of zeolite strongly influences the reaction chemistry, as in case of other type of catalysts usually H₂/CO molar ratios lower than 1 were observed (Table 4.4).

In general, all authors stated that the type of applied support has a significant influence on the state of nickel species on the catalyst surface. The strong interactions between support and active phase may result in the formation of inactive phases in DRM reaction, such as NiAl₂O₄ or MgO-NiO solid solution. On the other hand, too weak interactions between nickel species and their carrier promoted deactivation via sintering and formation of carbon deposits. From, discussed articles it may be concluded that the most beneficial effect on the catalyst activity is connected to mixed Al₂O₃-MgO support, which shows interactions between Ni phase and support of moderate strength and is characterized by high basicity.

4.3.2.2 The role of promoters

Suitable promoters are added to the catalyst in order to enhance its stability, selectivity and/or catalytic activity. The influence of a promoter on catalyst stability and activity may be explained by their ability to modify catalyst structure (type of active sites, additional sites). In DRM
reaction, the application of different types of promoters is usually aimed at increasing catalyst stability rather than its activity. In general, the promoters in DRM reaction may be divided into three groups: (I) alkali or alkaline earth metals, such as K, Li, Mg, Ca, Ba, (ii) rare earth metals, such as Ce, Zr, La and (III) other metals, such as Au, Ag, Sn, Bi, As, Pb and Cu.

Alkali or alkaline earth metals are applied because of their basic properties, which enhance catalyst affinity towards CO₂, and thus can help to oxidize carbon deposits. Moreover, they can form solid solution with NiO, increasing in this way the interactions between the support and active phase, and thus resulting in the formation of small nickel crystallites upon reduction with H₂, as well as suppresses coking. Rare earth metal oxides (e.g. CeO₂ or ZrO₂) on the other hand, exhibit redox properties, and thus also promote oxidation of carbon deposits. Other metals can be also added to the catalyst and their role is to either modify existing active sites or to create new active sites, and form in this way a bimetallic catalyst. The role of promoter can differ depending on the amount applied, type of support and method of a promoter introduction. Large amounts of promoters usually decrease catalytic activity due to the coverage of active sites [87]. Tables 4.6 and 4.7 present short review of different promoters applied in DRM reaction over Ni-based catalysts.

Promoter	Loading (wt.%)	Support	Ni (wt.%)	Effect of promoter addition	Ref.
			ALK	(ALI METALS	
К	1, 5, 10	γ -Al ₂ O ₃	20	Divides Ni surface into smaller ensembles; supress carbon deposition;	[144]
К	0.2-5	γ -Al ₂ O ₃	10	Partially blocks Ni active sites, Promotes coke gasification; Decreases activity	[145]
К	0.125 ¹	MgO	nd	Supress dissolution of carbon atoms in Ni crystallites; Decreases activity; Increases stability;	[89]
K, Li	0.5	CeO ₂	10	Improves stability, decreases activity and H ₂ /CO molar ratio; K can block Ni active sites; K catalyses C gasification	[140]
Mg	3	γ -Al ₂ O ₃	5, 10, 15, 20	Increases basicity of support; increases stability of the catalysts	[105]
Mg	2 E E		15	Increased Ni dispersion; Decreased activity towards CH ₄	[146]
Са	2.3, 5	Al ₂ O ₃	10	Increased Ni dispersion; Increased activity; Improved stability	
Са	10 ²	γ -Al ₂ O ₃	17	Increases activity and stability	[147]
Ва	nd	AI_2O_3	10	Improves reducibility of Ni; Inhibits formation of NiAl ₂ O ₄ spinel	[148]

Table 4.6 The effect of alkali and rare earth metal promoters on Ni-based catalysts in dry methane reforming.

Promoter	Loading (wt.%)	Support	Ni (wt.%)	Effect of promoter addition	Ref.
			RARE	EARTH METALS	
Ce	7	MgO	10	Improves Ni dispersion, Improves stability, increases activity	[93]
Ce	1, 5, 10	AI_2O_3	5	Increases activity towards CH ₄ , Improves stability	[87]
Ce	3	AI_2O_3	11.5	Improved dispersion of Ni particles; Decreased activity;	[149]
Ce	3, 5, 10	montmo rmolonit e	10	Increases activity and stability	[114]
Ce	6	SBA-15	5	Improved catalyst activity	[150]
CeO ₂ - ZrO ₂	10	SBA-15	10	Improves stability, decreases activity towards CO ₂	[100, 151]
Zr	1, 2, 3, 4, 5, 6	clinopti olite	8	Improves stability	[111]
Zr	1	α -Al ₂ O ₃	2	Promotes gasification of carbon deposits; Improves stability	[152]
Zr	5	SiO ₂	10	Enhanced reducibility; Improved catalytic activity;	[153]
La	0.25-15	SiO ₂	10	Increased dispersion of Ni; Improved interactions between Ni and SiO ₂ ; Improved stability and activity	[154]

Table 4.6 Continuation

 1 K_{at}/Ni_{at}=0.125;

² mol %

nd – no data

Osaki et al. [144] studied the effect of potassium addition into Ni/Al₂O₃ catalyst. The studies revealed that K⁺, due to its basic character, enhances adsorption of CO₂. However, the rate of CO₂ dissociation into CO and oxygen was not affected, suggesting that the increased stability of the catalyst was not caused by oxidation of carbon deposits through enhanced CO₂ adsorption. The obtained results showed that potassium was present on the nickel crystallites and divided them into smaller ensembles, thus nickel crystallites were too small to catalyse carbon-forming reactions. The coverage of nickel crystallites by potassium resulted also in decreased activity due to the blockage of active sites. Similar conclusions were drawn by Juan-Juan et al. [145] and Frusteri et al. [89], who investigated K-promoted Ni/MgO catalyst. Their studies showed that K addition resulted in electronic enrichment on the active sites and led to stronger interactions between Ni atoms and electron-acceptor oxygen intermediates adsorbed on the catalyst surface. This prevented dissolution of C atoms and as a consequence their nucleation and formation of carbon deposits.

The addition of potassium decreased catalytic activity but largely improved catalyst stability. Such effect was also observed for both K and Li promoted Ni/CeO₂ catalyst [140].

Magnesia was tested as a promoter for nickel supported on alumina by several authors [105, 146, 149, 155]. Generally, small additions of magnesium had double promotion effect. Firstly, it modified Ni-particles arrangement, due to the formation of MgAl₂O₄ spinel phase and the suppressed formation of inactive NiAl₂O₄. This can be ascribed to the fact that basic MgO is preferably reacting with acidic Al₂O₃, thereby inhibiting the reaction between NiO and alumina. Secondly, magnesia inhibited agglomeration of coke deposits by an effective CO₂ gasification. Both effects resulted in increased catalyst stability. However, the initial activity of catalyst was reported to be lower than for the unpromoted catalyst.

Sengupta et al. [146] compared Ni/Al₂O₃ catalyst promoted with Mg and Ca. The addition of Ca was more beneficial than Mg promotion, as the catalytic activity towards CO₂ and CH₄ and catalyst stability were improved for Ca-promoted material with respect to Mg-promoted and unpromoted catalysts. Catalysts characterization revealed that the Ca addition resulted in the formation of new active sites able to adsorb H₂ and CO₂. At the same time Mg had negative effect on CO₂ and CH₄ conversion. The beneficial effect of Ca addition into Ni/Al₂O₃ catalyst were also observed by Zhang et al. [147].

The application of Ba as a promoter to Ni/Al_2O_3 was investigated by Garcia-Dieguez et al. [148]. A small addition of barium did not influence catalyst activity or stability. However, it inhibited the formation of $NiAl_2O_4$ spinel phase, and thus improved reducibility of nickel species.

CeO₂ is one of the commonly used promoters in DRM reaction. Wang et al. [87] tested Ni/Al₂O₃ catalyst promoted with 1 to 10 wt.% Ce. The addition of Ce improved catalyst stability regardless of Ce content with respect to unpromoted catalyst, as with increasing content of Ce Ni dispersion increased as well. Similar observation was made by Yan et al. [149]. Moreover, the addition of CeO₂ prevented the formation of inactive NiAl₂O₄ phase and enhanced reducibility of the catalyst. The results of TG experiments after reaction revealed that the catalyst resistance to coking was increasing with the increasing content of ceria. Nevertheless, the authors stated that the optimal content of Ce addition should be between 2-5%, as some blockage of active sites could occur. Similar results were reported for Ni/MgO catalyst [93].

Studies carried out by Kaydouh et al. [150] showed the importance of the preparation method on the catalyst activity. The effect of order of Ni and Ce introduction into SBA-15 by impregnation method was investigated. When Ce was impregnated prior to Ni, the catalyst showed much better performance than in case when nickel was deposited first. The increased activity of the catalyst prepared by the former procedure was ascribed to the formation of smaller Ni crystallites.

Promoter	Loading (wt.%)	Support	Ni (wt.%)	Effect of promoter addition	Ref.
Со	4	CeO ₂	8	Improved stability by formation of easily oxidized carbon deposits	[76]
Со	3.75	CeO ₂	3.75	Increased activity and selectivity; Inhibits formation of carbon	[156]
Со	3.5	ZSM-5	3.5	Improved activity and selectivity; Inhibited formation of carbon	[157]
Cu	1	SiO ₂	8	Increased catalytic activity and stability. Stabilized Ni active sites; Inhibited deactivation by CH₄ decomposition;	[158]
Fe	2	CeO ₂ - ZrO ₂	3	Increased activity; Catalyst quickly deactivated	[159]
Ag	0.3, 0.6, 2.4*	CeO₂	10*	Lowered activity of Ni surfaces; promotes RWGS; Accelerated combustion of coke deposits	[94]
Pt	0.3	MgO	5	Improved catalytic activity, selectivity and stability	[160]
Pt	0.4	AI_2O_3	10	Increased activity	[161]
Pt	1	AI_2O_3	6	Improved activity and selectivity; Inhibited formation of carbon whisker-like deposits	[162]
Rh	0.5	CeO ₂ - ZrO ₂	4.5	Increased activity and stability;	[159]

Table 4.7 The effect of introduction of a second metal to Ni-based catalyst in DRM reaction.

*mol %

Nd – no data

Zirconia addition onto various Ni supported catalyst has been studied [111, 152, 163]. In general, it has been reported that zirconia addition enhances reducibility of nickel species, leading to higher activity of the catalyst [111, 152, 153]. Promotion by Zr had also a positive effect on catalyst stability for nickel supported on alumina and clinoptolite catalysts. On the other hand, Yao et al. [153] observed monotonic decrease in catalyst activity over Zr-promoted Ni/SiO₂ catalyst, which was caused by deposition of carbon deposits. The deactivation of catalyst was more evident at lower temperatures.

Albarazi et al. [100, 151] promoted Ni/SBA-15 catalyst with ceria-zirconia, which was well dispersed inside pores of the support, creating in this way a micro-mesoporous catalytic system with a beneficial effect on DRM reaction. The promoted catalyst exhibited higher activity towards

CH₄, and its stability was also enhanced. However, the activity towards CO₂ was slightly lower than for the unpromoted catalyst.

Zhu et al. [154] studied addition of La, Mg, Zn and Co into Ni/SiO₂ catalyst. The best performance was observed for 5wt.% La promoted catalyst, which exhibited excellent stability in DRM reaction within 30h. Similar stability was shown by Zn promoted catalyst. The high activity and stability for the former were attributed to high dispersion of small nickel crystallites on the support surface. Mg and Co addition did not improve catalyst stability significantly. The authors also observed that Mg and La addition decreased the contribution of RWGS reaction, increasing H₂/CO molar ratio.

Ay and Uner [76] investigated Ni, Co and Ni-Co ceria supported catalysts in DRM. Their results showed no beneficial influence of Co incorporation into Ni/CeO₂ in terms of CH₄ and CO₂ conversions. Both Ni/CeO₂ and Ni-Co/CeO₂ catalysts showed very similar activity. The loss in CH₄ and CO_2 conversions was observed at the beginning of the reaction. It was attributed to the deactivation of catalysts by carbon-forming reactions. However, the addition of Co into Ni/CeO₂ resulted in formation of less stable carbon deposits (lower temperature of oxidation of carbon deposits). It should be added that Co/CeO₂ sample exhibited very low activity compared to Ni and Ni-Co containing catalysts. The authors explained it by general lower activity of Co towards DRM and strong interactions of Co with the support. A thin layer of ceria over active metal crystallites was observed on TEM images, pointing to the blockage of active centres of DRM reaction for both active catalysts. On the other hand, increased catalytic activity in DRM was observed by Luisetto et al. [156] for Ni-Co bimetallic catalyst. Their research showed that Co-Ni alloy was formed on the catalyst surface. It modified catalytic properties of the material, and thus increased activity, selectivity and stability. Beneficial effect on catalytic activity of Co-Ni bimetallic catalyst supported on ZSM-5 zeolite was observed also by Estephane et al. [157]. The bimetallic catalyst showed higher activity and was more stable than monometallic nickel catalyst. It was attributed to a synergetic effect of cobalt on nickel species, and Co played a role of oxidation catalyst for the removal of catalytic coke.

Chen et al. [158] reported that the addition of Cu into Ni/SiO₂ catalyst significantly increased its stability. The copper addition stabilized the structure of active nickel sites on the catalyst surface, thus preventing the loss of catalytic activity by sintering of nickel species. Moreover, Cu inhibited deactivation arising from CH₄ decomposition reaction. Cu-Ni species which were formed on the catalyst surface, suppressed the formation of inactive carbon deposits during DRM reaction.

Yu et al. [94] studied the promotion of Ni/CeO₂ catalyst with Ag. This addition decreased the activity of the catalyst due to the partial blockage of Ni active sites, but significantly increased stability within 100h catalytic tests. The characterization of the catalyst showed that Ag species were present on the step sites on Ni surface and a part of Ag species was bonded with ceria support. The promotion with Ag also changed the type of catalytic coke from graphitic or whisker carbon to amorphous carbonaceous deposits, which may play an active role in DRM reaction and are easier to oxidize than graphitic carbon.

Small additions of Pt were reported to have a very beneficial effect on the performance of Ni-based catalyst in DRM reaction [160-162]. Ni-Pt catalysts supported on MgO or Al₂O₃ exhibited improved catalytic performance, higher selectivity towards H₂/CO molar ratio and minimal deposition of carbon deposits. Gould et al. [162] observed that no whiskers-type of carbon deposits were formed for the Pt-Ni catalyst supported on Al₂O₃ which was prepared by atomic layer deposition method. The enhanced catalytic performance of bimetallic catalyst was attributed to the fact that Ni-Pt surfaces formed Ni-terminated surfaces which were associated with higher DRM rates than Pt-terminated surfaces. Presence of Pt on the edges of Ni crystallites inhibited carbon diffusion and thus resulted in higher resistance for coking.

Koubaissy et al. [159] reported that Rh addition into Ni/CeO₂-ZrO₂ catalyst enhanced its stability and catalytic activity. However, carbon deposits were still present on the catalyst surface after DRM catalytic test. Thermogravimetric experiments revealed that the addition of Rh had influenced the type of carbon deposits formed during DRM reaction and resulted in the formation of amorphous active carbon, which did not decrease conversions of CH₄ and CO₂.

Effects of the different promoters on the similar nickel supported catalysts were tested by several authors in order to find out the best promoter [164-166]. Choi et al. [164] investigated the effect of 2wt.% Co, Cu, Zr, Mn, Mo, Ti, Ag or Sn on catalytic activity of nickel supported on commercial ICI 46-1 material composed of 13wt.% CaO, 6.5% K₂O, 12% MgO and Al₂O₃. The carrier contained high amounts of alkali oxides, and thus exhibited high basicity. The catalytic activity of the tested materials followed the sequence for promoters: Co, Cu, Zr > unpromoted catalyst > Mn > Ti > Mo > Ag > Sn. Although the catalysts promoted by Co, Cu and Zr exhibited higher activity, high amounts of carbon were formed during the DRM reaction. On the other hand, the addition of Mn, Mo and Ag resulted in good resistance to coking. It must be mentioned, however, that only in case of the Mn-promoted sample registered conversions of CH₄ and CO₂ were similar to those for unpromoted catalyst. This is why the authors stated that the best promotion effect was obtained for manganese. Castro Luna et al. [165] studied Ni/Al₂O₃ catalysts promoted by 0.5wt.% of K, Ca, Mn or Sn. The DRM tests carried out at 750°C for 30h showed that the addition of promoters decreased catalytic activity with respect to the unpromoted sample. Moreover, only for the catalysts doped with K or Ca stable values of CH₄ and CO₂ conversions were registered, suggesting that samples did not exhibit deactivation. The performance of the tested catalysts followed the sequence: unpromoted catalyst > K > Ca > Sn > Mn.

The effect of Co, Ca, K, Ba, La, Mn or Ce promotion of Ni/MgO-ZrO₂ catalyst was studied by Fan et al. [166]. The activity of the prepared materials tested in DRM reaction at 750°C decreased in the order Ni-Co > Ni-La \approx Ni-Ce > Ni-Ba > Ni-Mn > Ni-K > Ni-Ca. The best performance of Ni-Co catalyst was attributed to the Ni-Co solid solution which reduced coke formation and improved catalytic conversion. Ni-La and Ni-Ce catalysts showed similar performance. The activity of Ni-Ba and Ni-Mn catalyst dropped within 40h TOS. On the other hand, a fairly stable performance was shown by Ni-K and Ni-Ca catalysts. The activity sequence followed that of metal dispersion. Carbon deposits were present on all catalysts after 40h catalytic tests and the highest amount was registered for Ni-Mn catalyst.

4.3.2.3 Conclusions

The presented review of nickel based catalysts showed that the catalytic performance of materials in DRM reaction is dependent on a number of factors. It is rather hard to establish the best support and promoter, as reported materials were tested under different conditions, with different loadings of metals and were prepared by different methods. Nevertheless, general trends in catalysts for DRM process can be established.

Researchers are focusing on preparing materials with high dispersion and small size nickel particles, which can be achieved by increasing interactions between nickel species and support. On the other hand, too strong interactions can significantly decrease reducibility of nickel species, and thus have negative effect on activity. Moderate interactions between Ni and support with high dispersion of stable nickel species were reported for MgO-Al₂O₃ support (Table 4.4, 4.5).

The addition of promoters can drastically change catalytic properties of a material. The positive effect of basic oxides and materials with high oxygen storage capacity is stressed in literature. Another concept is to introduce a second metal into catalytic systems, in order to create synergetic effect between Ni and other metal species, and inhibit in this way coking, as well as increase material activity. However, the effect of promotor addition is dependent on the used support, preparation method and promoter loading (Table 4.6, 4.7).

4.4 Reaction Mechanism

The mechanism of dry reforming of methane have been studied by a number of research groups [97, 139, 167-175]. The earliest proposal of reaction mechanism was published in the 60s of last century [44]. DRM mechanism was proposed to be similar to that of steam reforming, as water is also present in DRM reaction (formed via RWGS) and operating conditions are similar. Since this time the number of papers on DRM reaction mechanism based on theoretical calculations and experimental analysis has increased significantly.

In general, two reaction paths are proposed, which include Eley-Rideal or Langmuir-Hinshelwood mechanism (Table 4. 8). The mechanisms presented in Table 4.8 show general reactions steps and do not consider formation of various other intermediate species. In Eley-Rideal mechanism one reactant (CH₄ or CO₂) is assumed to be associatively adsorbed on the catalyst surface. The species formed via dissociative adsorption of first reactant are subsequently reacting with second reactant from the gas phase, leading directly to products. The latter is considered as a rate-determining step [174].

The Eley-Rideal model of the reaction mechanism is less popular than Langmuir-Hinshelwood mechanism, and there is a larger number of papers based on the latter. In the Langmuir-Hinshelwood mechanism, adsorbed CH_4 molecules are decomposed to CH_x species and hydrogen. CO_2 adsorbed on the catalyst surface undergoes dissociation producing CO and adsorbed oxygen species. Oxygen species can react with CH_x species leading to H_2 and CO.

Table 4.8	Mechanism	of dry	reforming	reaction	[174]
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Eley-Rideal mechanism	Langmuir-Hinshelwood mechanism
ER I	$CH_4 \rightleftharpoons CH_4^*$
$CH_4 + * \rightleftharpoons CH_4^*$	$CH_4^* \rightleftharpoons CH_x^* + (4-x)/2 H_2$
$CH_4*+CO_2 \rightleftharpoons 2CO + 2H_2 + *$	$CO_2 \Rightarrow CO_2^*$
ER II	$CO_2^* \Rightarrow CO + O^*$
$CO_2 + * \rightleftharpoons CO_2^*$	$CH_x^* + O^* \rightleftharpoons x/2 H_2 + CO$
$CO_2^* + CH_4 \rightleftharpoons 2CO + 2H_2 + *$	

*catalyst active site

Density functional theory (DFT) method has been used by many authors in order to establish the mechanism of CO_2 reforming of methane on Ni(111) planes [169-171, 173]. The schematic representation of the resulting mechanism is presented in Fig. 4.3. First methane is adsorbed on Ni active sites, and then it undergoes sequential dissociation into surface CH_x species

 $(CH_4 \Rightarrow CH_3 \Rightarrow CH_2 \Rightarrow CH)$ and surface H atoms. At the same time, CO_2 undergoes dissociation on the catalyst surface into CO and surface O species. In the next step, adsorbed CH_x species can be oxidized to CH_xO . Moreover, the calculations confirmed that oxidation is more favoured than dissociation into C and H. Oxidized CH_xO species subsequently decompose to CO and surface H. Mobile H atoms on the catalyst surface can form H_2 .



Fig. 4.3 Mechanism for dry reforming of methane on Ni catalyst proposed by Zhu et al. [173] (with the permission of Elsevier).

Theoretical studies performed by Wang et al. revealed that in DRM reaction on Ni(111) surfaces CO species are strongly adsorbed, which results in the accumulation of CO on the catalyst surface and hinders subsequent reactions, and thus promotes the formation of carbon deposits via Boudouard reaction. It may be therefore concluded that the research on the DRM catalyst should be focused on the promotion of CO desorption.

The stability of a catalyst in the proposed mechanism is also dependent on the presence of surface H and O atoms, which can help to eliminate carbon deposition. Surface H atoms are more active than O species, which can explain why lower amounts of catalytic coke are formed during SRM than DRM process. Wang et al. [170, 171] additionally proposed that the rate-limiting step in DRM mechanism on Ni(111) surfaces is CH_4 dissociation into CH_x species. On the other hand, calculations carried out by Zhu et al. [173] showed, that this is the case only at low temperatures, at high temperatures the rate-determining step is oxidation of CH_x species. The formation of CH_3OH and HCOOH was proven to be less favourable than H_2 and CO, which explains high selectivities for syngas obtained over nickel-based catalysts.

Although DFT studies provide very useful information about reaction mechanism, they do not show the complete picture. Reported results showed that carbon and water formation is not favourable on Ni(111) surfaces [170, 171], while in real reaction conditions these reactions proceed easily on other Ni planes, resulting in catalyst deactivation. CH₄ decomposition was reported to be surface sensitive and proceed more easily on Ni(100) and Ni(110) surfaces [73, 169]. Water, on the other hand, is formed via RWGS which accompanies DRM reaction [88, 91, 138, 140]. Moreover, in theoretical studies the effect of the support is not included. Ferreira-Aparicio et al. [172] showed that the mechanism of DRM reaction over Ru/Al₂O₃ is highly influenced by the presence of alumina surface hydroxyl groups. Thus, experimental investigations of reaction mechanism provide more accurate results.

Kroll et al. [168] investigated DRM mechanism on Ni/SiO₂ catalyst. Their results showed that during the first step of reaction, CH₄ was decomposed on the Ni surface to C and H₂. The C atoms formed with nickel species carbide-like monomer, which created new active sites for DRM reaction. The accumulation of this carbide-like active species resulted in the formation of carbon whiskers or carbon veils. Methane dissociation proceeded fairly fast. The rate-limiting step was oxidation of adsorbed surface carbon by oxygen atoms, the latter formed via dissociation of CO₂. This reaction requires migration of surface O and C atoms and surface diffusion was expected to be unflavoured at high temperatures. Adsorbed H and O atoms might produce water.

Based on the literature review of the experimental data [97, 139, 168, 174-176], the mechanism of DRM reaction over Ni catalyst, based on Langmuir-Hinshelwood model can be described by four consecutive steps:

- Step 1. Adsorption of methane on the Ni active site and its dissociation to produce surface hydrogen and hydro-carbonate species. This step is considered a relevant kinetic step.
- Step 2. Adsorption of CO₂ on nickel active site or basic support surface to form carbonate (CO₃²⁻) and/or bicarbonate (HCO₂⁻) species, which is followed by direct CO₂ dissociation to CO and O. The produced O surface atoms can combine with H to form OH groups. The dissociation of CO₂ can be assisted by H surface atoms

producing in this way CO and OH groups. This reaction participates in DRM mechanism through RWGS reaction.

- Step 3. The surface hydroxyl groups of the support react with adsorbed CH_x species and formate-type intermediate species are produced. CH_xO species are subsequently decomposed to H₂ and CO. A support may play a very important role in this reaction step as it can be considered a sink for hydroxyl surface groups. Therefore active site for the formation and decomposition of CH_xO species may be at the metal-support interface.
- Step 4. CH_xO intermediates can be also formed via reaction of surface O atoms originating from CO₂ dissociation and CH_x species.

The rate-determining step in the proposed general mechanism of DRM reaction can differ depending on the nature of a catalyst and reaction conditions. Generally there is no single rate-determining step in methane reforming. The review on the DRM kinetics prepared by Kathiraser et al. [174], showed that in the proposed mechanism of DRM reaction the following elementary steps were considered as rate limiting: surface activation of methane on Ni species, surface reaction between O or OH, surface reaction between O and CH_x, carbon oxidation, reverse Boudouard reaction or CO₂ dissociation.

4.5 Applications of DRM

4.5.1 Industrial experience with large scale reforming of CO₂-rich gas

The industrial applications of dry reforming process are so far limited to a combination of steam reforming and dry reforming reactions. The addition of CO₂ into a feed allows to control distribution of obtained products, i.e. H₂/CO molar ratio. Depending on the subsequent application of obtained synthesis gas, processes differ in operating parameters and feed composition. The comparison of different large-scale reforming processes which apply CO₂-rich gas is compared in Table 4.9 [177].

		Operating co	Inditions			Primary re	former feed		Outlet	
Process	Catalyst	Feed	P (Bar)	Т _{ЕХІТ} (°C)	H₂O/СН₄ (-)	CH₄ (mol %)	CO ₂ (mol %)	H ₂ (mol %)	H ₂ /CO (-)	TOS (h)
HOU-1	Ni/MgAl ₂ O4	Natural Gas	23	945	1.4	74	18	6	2.6	400
HOU-2	Ni/MgAl ₂ O4	Natural Gas	24	945	1.6	56	44	0	1.8	380
Iran	Ni/MgAl ₂ O4	Natural Gas	20	096	1.3	70	12	17	3.0	ı
Indonesia	Ni/MgAl ₂ O4	Natural Gas	12	096	2.1	74	23	2	2.7	ı
Malaysia	Ni/MgAl ₂ O4	Natural Gas	25	950	1.5	63	20	16	2.7	ı
South Korea	Ni/MgAl ₂ O4	Naphtha	25	006	1.7	47	38	15	2.1	ı
India	Ni/MgAl ₂ O4	Naphtha	22	920	1.7	40	41	17	1.9	ı
ЯЛ	Ni/MgAl ₂ O4	Naphtha	20	006	2.0	32	56	12	1.7	ı
Netherlands	Ni/MgAl ₂ O4	Natural Gas	15	815	2.0	28	71	1	1.2	ı
			Ś	ulphur-Passivateo	d ReforminG (SP/	ARG):				
HOU-3	Ni/MgAl ₂ O4	Natural Gas	9	890	1.0	57	37	9	1.9	500
HOU-4	Ni/MgAl ₂ O4	Natural Gas	9	630	0.4	40	59	1	0.9	500
HOU-5	Ni/MgAl ₂ O4	Natural Gas	14	930	0.7	38	61	1	0.9	160
USA	Ni/MgAl ₂ O4	Natural Gas	7	006	0.9	61	33	9	1.8	ı
HOU-7	Ru/MgAl ₂ O4	Natural Gas	32	940	0.9	51	44	ß	1.4	490
Japan	Ru/MgAl ₂ O ₄	Natural Gas	2	850	1.8	10	56	32	1.0	

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In a typical large-scale combined SRM-DRM reforming plant, feedstock, which may be composed from lean natural gas to heavy naphtha, is first heated to ca. 400°C and undergoes desulphurization process in order to remove sulphur species. Higher hydrocarbons which may be present in the feed, are converted into a mixture of H₂, CO₂, CH₄ and traces of CO in a pre-reformer. This stage is usually realized in the temperature range 400-550°C in order to avoid deactivation by carbonaceous deposits from higher hydrocarbons. In the next stage, the feed gas is introduced into a tubular reactor where actual reforming takes place and a mixture of CH₄/CO₂/H₂O is converted into synthesis gas. The reactor tubes are placed in the furnace powered by the combustion of fuels to supply heat for endothermic reforming process. The temperature in the reformer may differ, depending on the process. Usually it is performed at high temperatures, up to 1000°C.

The commercialization of such reforming plants is dependent on carbon-free operation. It is essential because of the problems connected with high pressure drop or expensive costs of loading of a new batch of catalyst. As it can be seen from Table 4.9, so far, large-scale reforming plants apply nickel catalyst supported on alumina-magnesia. This, clearly points that the search for a catalyst for DRM reaction should be focused on similar systems.

The two most often mentioned in literature large-scale reforming technologies, which apply DRM reaction, are CALCOR and SPARG processes [34].

4.5.1.1 CALCOR process

The production of carbon monoxide realized via CALCOR process combines SRM with DRM. The first pilot plants which applied this process were built in the 40s of the last century [178]. Laboratory scale studies carried out by Reitmeier et al. [178] showed that it is possible to obtain synthesis gas with high excess of CO (H_2 /CO around 0.5) by a combination of steam and dry reforming reactions without any difficulties arising from the deposition of carbon. Currently, CALCOR process is a well-established technology for production of pure CO, which can be further utilized on-site for the conversion to organic compounds, such as phosgene.

In CALCOR process carbon monoxide is obtained by steam reforming of natural gas mixed with recycled CO₂ at high temperatures and high pressures in the presence of an undisclosed catalyst. It is believed, that high resistance to coking in CALCOR process is obtained via application of a few catalysts with various activities and shapes, which are placed in a different parts of reformer tubes. The process requires highly cleaned feed in order to protect the catalysts from sulphur poisoning. Usually in standard CALCOR process syngas with H₂/CO molar ratio around 0.42 is obtained [179]. The required heat comes from the combustion of fossil fuels and tail gas from CO purification units. It should be mentioned, however, that the application of DRM reaction in

CALCOR process does not result in CO_2 emissions reduction. The analysis showed that for every ton of CO produced, ca. 1.8 tons of CO_2 is emitted to the atmosphere.

4.5.1.2 SPARG process

Sulphur Passivated Reforming (SPARG) process was commercialized in 1987 [34]. It combines steam and dry reforming with the aim to obtain synthesis gas with H₂/CO molar ratio around 1.8, which can be further used to produce acetic acid, dimethyl ether or oxo-alcohols. SPARG utilizes nickel-based catalyst, which resistance to coking was increased by passivation of nickel surface by sulphur. In this way active sites for carbon-forming reactions are poisoned, while catalytic activity towards reforming is maintained ('promotion by poisoning') [180]. The poisoning of Ni active sites is performed by co-feeding small amounts of H₂S and H₂ and needs to be carried out carefully in order to avoid the formation of nickel sulphides, which inhibit catalyst activity towards SRM/DRM [177]. SPARG process proceeds at high temperatures around 1000°C.

4.5.2 Potential future applications of DRM reaction

4.5.2.1 Chemical Energy Transmission and/or Storage Systems (CETS)

Dry reforming reaction may be applied in exothermic-endothermic reaction-cycle systems for transport and storage of energy. The schematic concept of the so called chemical energy transmission systems is presented in Fig. 4.4. Endothermic reaction is powered by fossil, nuclear or renewable energy. The products of the reaction, which store energy, are saved for later use or transported through pipelines to a location where exothermic reaction releases energy [167].

So far several concept of this CETS system has been considered for industrial application. The most advanced developments have been made in the nuclear ADAM-EVA process [167]. The application of DRM reaction is CETS systems has a huge potential. McCrary et al. [181] and Chubb [182] proposed SOLCHEM technology. In this concept, reversible closed-cycle chemical reactions are carried out in order to transport solar energy from solar collectors to a central station, where the energy could be released in case of increased demand. The process investigated CO₂ reforming-methanation cycle, in which a mixture of CH₄ and CO₂ underwent dry reforming reaction at temperatures higher than 700°C, giving H₂ and CO. The energy for the DRM reaction was supplied from the solar collectors. Obtained syngas can be transported and subsequently undergoes methanation at temperatures below 600°C, to form methane and carbon dioxide. The stored energy is released in this exothermic reaction. Although, the SOLCHEM concept has not been developed on the industrial scale, it proposes an alternative way to use DRM reaction as an energy carrier.



Fig. 4.4 The scheme of chemical energy transmission system (CETS) for transport and storage of energy

Similarly as proposed in SOLCHEM technology, DRM reaction can be powered by other renewables or nuclear energy. The only limitation concerning the application of DRM in CETS is the offer of a stable catalyst.

4.5.2.2 DRM for production of chemicals

Apart from the application of DRM as a way of transport and storage of energy, the main potential future application of this process is associated with the production of synthesis gas to be used in subsequent synthesis of fuels or chemicals. It has been proven that there is a need on the market for synthesis gas with H_2/CO molar ratio lower than that obtained via SRM process [177]. In this way not only added-value products could be obtained, but also CO_2 emissions could be reduced.

Ross et al. [48] analysed CO_2 mitigation connected with potential future applications of DRM reaction as the means of producing hydrocarbons via FT synthesis, methanol and carbon (via reduction of CO). The results presented in Table 4.10, showed that the combination of DRM and SRM could attribute to the reduction of CO_2 emissions, if powered by non-fossil fuel energy source. The application DRM process alone might be thus even more beneficial.

The main problem limiting the application of DRM reaction is the formation of carbon deposits on the catalyst surface. Therefore, the commercialization of DRM reaction on industrial scale is depended on the offer of new stable and active catalyst and price of ton of CO₂ (around 8€ nowadays).

Route	Moles of CO ₂ mitigated per mole of CO ₂ consumed	Conclusions		
CH ₄ to higher hydrocarbons (HC)				
Reactions:				
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	A net reduction of	This is an effective method of CO ₂		
$CH_4 + H_2O \Rightarrow CO + 3H_2$		intigation		
$6\text{CO} + 13\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{12} + \text{H}_2\text{O}$				
CH₄ to methanol				
Reactions:		Provides a trap for some CO ₂ . The methanol production by combined		
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	A net reduction of 0.66 moles of CO ₂	SRM-DRM process will contribute		
$CH_4 + H_2O \Rightarrow CO + 3H_2$		only to small global CO ₂ emissions		
$CO + 2H_2 \rightleftharpoons CH_3OH$		reduction.		
CH₄ to carbon				
Reactions:	A net reduction of	Offers an energy efficient means of		
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	1 mole of CO_2	as adsorbent or as catalyst support.		
$2CO + 2H_2 \rightleftharpoons 2C + 2H_2O$				

Table 4.10 The comparison of different concepts of CO_2 conversion to varied products, implementing DRM reaction(adapted from [48])

5 Hydrotalcites and hydrotalcite-derived materials

Layered/lamellar materials thanks to their specific properties and bi-dimensional structure found applications in catalytic and adsorption technologies. The first hydrocracking process developed over 90 years ago was based on acid-treated clays [183]. Since then, research on these type of materials has been largely developed and resulted in a large spectrum of textural, compositional and structural modifications of layered materials. Thanks to such modifications it is possible to tailor properties of these materials, which makes them very interesting for catalysis.

All lamellar solids may be divided into three groups depending on the charge of the layers [183, 184]:

- Natural layer materials, such as graphite, metallic oxides (V₂O₅), hydroxides brucite (Mg(OH)₂), phosphates.
- Negatively charged layers with compensating cations in the interlayer space cationic clays (clinoptilolite, montmorillonite, vermiculite, hectorite). These type of materials occur widely in nature. Their layers are formed by the association of two or several octahedral and tetrahedral sheets, generally around Al and Si atoms, respectively.
- Positively charged layers with compensating anions anionic clays (hydrotalcitelike materials). In contrast to cationic clays these types of materials are rarely present in nature, and thus typically they are produced in the laboratory.

This chapter is focused on the anionic clays, layered double hydroxides (LDHs) or hydrotalcite-like materials (HTs), methods of their synthesis and modifications, their physicochemical and catalytic properties, and, especially, activity of LDHs-derived materials in DRM reaction.

5.1 Structure and composition

Hydrotalcite is a naturally occurring layered mineral, discovered in Sweden in 1842, with chemical formula: $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ [185]. The name hydrotalcite is derived from the resemblance with talc ($Mg_3Si_4O_{10}(OH)_2$), and high water content of the mineral. Similarly as talc, hydrotalcite mineral can be easily crashed into a white powder. Hydrotalcite occurs in nature in foliated and contorted plates and/or fibrous masses [185].

Hydrotalcite is a mixed magnesium and aluminium hydroxycarbonate, which possesses the structure of brucite i.e. magnesium hydroxide Mg(OH)₂. Hydrotalcite layers are built of octahedral units in which divalent or trivalent cation is placed in the centre of an octahedron and six OH⁻ groups are placed in the corners of the octahedron (Fig. 5.1). Similarly as in brucite, octahedral units are linked by edges, forming in this way parallel layers. Depending on the arrangement of the layers, hydrotalcite structure may have rhombohedral or hexagonal symmetry, in which the unit cell is build up from three and two hydrotalcite layers, respectively. For both naturally occurring and synthetic hydrotalcites rhombohedral symmetry is more common [185-188].



Fig. 5.1 The octahedral unit of brucite-like layers in hydrotalcite structure



Fig. 5.2 The schematic representation of the hydrotalcite structure

In hydrotalcite brucite-like layers a part of divalent magnesium cations have been isomorphously replaced by trivalent aluminium cations. Such substitution is possible because of similar ionic radii of Mg²⁺ and Al³⁺. Thanks to the substitution, brucite-like layers of hydrotalcite possess positive charge. This charge is compensated by carbonate anions present in the interlayer spaces. Water molecules fill the voids in the spaces between hydrotalcite layers [185-188]. A schematic representation of hydrotalcite structure is presented in Fig. 5.2.

			Fo	rmula	Unit cell			
Mineral	Laye	er comp	osition	Interlayer o	composition	paran	neters	Symmetry
	M ²⁺	M ³⁺	(OH)	Α	∙nH₂O	a (Å)	c (Å)	
Hydrotalcite	Mg_6	AI_2	(OH) ₁₆	(CO ₃)	·4(H ₂ O)	3.05	22.8	3R
Manasseite	Mg_6	AI_2	(OH) ₁₆	(CO ₃)	·4(H ₂ O)	3.10	15.6	2H
Stichtite	Mg_6	Cr_2	(OH) ₁₆	(CO ₃)	·4(H ₂ O)	3.10	23.4	3R
Desautelsite	Mg_6	Mn ₂	(OH) ₁₆	(CO₃)	·4(H ₂ O)	3.11	23.4	3R
Pyroaurite	Mg_6	Fe ₂	(OH) ₁₆	(CO ₃)	·4(H ₂ O)	3.11	23.4	3R
Takovite	Ni ₆	AI_2	(OH) ₁₆	(CO₃,OH)	·4(H ₂ O)	3.03	22.6	3R
Reevesite	Ni ₆	Fe ₂	(OH) ₁₆	(CO ₃)	·4(H ₂ O)	3.08	23.4	3R
Barbertonite	Mg_6	Cr ₂	(OH) ₁₆	(CO ₃)	·4(H ₂ O)	3.10	15.6	2H
Honessite	Ni ₆	Fe ₂	(OH) ₁₆	(SO ₄)	·4(H ₂ O)	3.08	26.0	-
Iowaite	Mg_6	Fe ₂	(OH) ₁₆	Cl_2	·4(H ₂ O)	3.12	24.3	3R
Meixnerite	Mg_6	AI_2	(OH) ₁₆	(OH) ₂	·4(H ₂ O)	3.04	22.9	3R

 Table 5.1 Minerals from hydrotalcite and manasseite group. (Data adapted from [185, 186])

After discovery of hydrotalcite, another mixed hydroxycarbonate of magnesium and iron was discovered. Shortly, a large number of minerals with different compositions but the same hydrotalcite-like structure were developed. Currently, the name hydrotalcite (hydrotalcite-like compounds - HTs, layered double hydroxides – LDHs) is used to describe a large group of naturally occurring minerals (Table 5.1) and synthetic materials, which possess layered structure of hydrotalcite. The general formula of such compounds can be represented as [186]:

$$[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}][(A^{n-}_{x/n})\cdot mH_{2}O]$$
 (eq. 5.1)

where: M^{2+} , M^{3+} - di- and tri-valent cations, A – interlayer anions, x – mole fraction of trivalent cations, the part $[M^{2+}_{1-x}M^{3+}_{x}(OH)]_2$ describes the composition of brucite-like layers and the part $[(A^{n-}_{x/n})\cdot mH_2O]$ describes composition of interlayer spaces.

Synthetic hydrotalcite-like materials can be easily prepared in the laboratory. In order to obtain a pure material, a few requirements need to be fulfilled. Firstly, there is a possibility of introducing different type of cations into HTs brucite-like layers. The di- and tri-valent cations which

can replace Mg^{2+} and Al^{3+} need to have ionic radii similar to those of magnesium and aluminium. The ionic radii of cations which can be introduced into hydrotalcite structure are presented in Table 5.2. Secondly, the molar ratio between di- and tri-valent cations, described by mol fraction of tri-valent cations x, needs to be appropriate. In general, it has been reported that x values between 0.2 and 0.33 guarantee the synthesis of pure hydrotalcite structure. However, successful synthesis of hydrotalcite with x in the range of 0.1-0.5 has also been reported [185]. The nature of cations introduced into brucite-like layers is another important factor. Excess of some cation can cause the formation of additional phase e.g. separate hydroxide. Cations such as Cu^{2+} , Ni^{3+} or Mn^{3+} , when introduced in high amounts, will form separate phases of carbonates or hydroxides thanks to Jahn-Teller effect, which involves the distortion of octaherda. Kannan et al. [189] reported that for Cu/Mg/Al-containing hydrotalcites, it is possible to obtain LDHs phase only when Cu^{2+}/Mg^{2+} is equal or lower than 1. The excess of Mg^{2+} stabilizes copper cations in an octahedral coordination of HTs lattice. In cases of Cu^{2+}/Mg^{2+} molar ratios higher than unity Jahn-Teller distortion causes formation of $CuCO_3$ phase.

Generally, di- and tri-valent cations are placed in the brucite-like layers of hydrotalcite. However, it is possible to introduce mono-valent and tetra-valent cations into the layers. To mention some examples, Pavel et al. [190] reported a successful synthesis of Li/Al hydrotalcite, Tichtit et al. [191] introduced Zr⁴⁺ and Velu et al. [192] Sn⁴⁺ cations into brucite-like layers.

Cation				lor	nic radii (n	im)			
M ⁺	Li⁺ 0.060								
N/12+	Mg ²⁺	Cu ²⁺	Ni ²⁺	Co ²⁺	Zn ²⁺	Fe ²⁺	Mn ²⁺		
	0.065	0.069	0.072	0.074	0.074	0.076	0.080		
N/13+	Al ³⁺	Ga ³⁺	Ni ³⁺	Co ³⁺	Fe ³⁺	Mn ³⁺	Cr ³⁺	V ³⁺	Ti ³⁺
IVI	0.050	0.062	0.062	0.063	0.064	0.066	0.069	0.074	0.076
N.44+	Ti ⁴⁺	Sn ⁴⁺	Zr ⁴⁺						
IVI	0.068	0.071	0.080						

Table 5.2 Ionic radii of different cations, which can be placed in hydrotalcite brucite-like layers (adapted from [185].

There is practically no limitation when it comes to the type of anions present in the HTs interlayer spaces. The most common anions present in the interlayer spaces are carbonates, which can be exchanged for other type of anions. This gives an opportunity of obtaining a variety of compositions for the interlayer domains. The following families of anions can be found in HDTs structure [185-188]:

Halides (F⁻, Cl⁻, Br⁻, l⁻),

- Non-metal oxoanions (BO₃³⁻, CO₃²⁻, NO₃⁻, Si₂O₅²⁻, HPO₄²⁻, SO₄²⁻, ClO₄⁻, AsO₄³⁻, SeO₄²⁻
 , BrO₄⁻ etc.),
- Oxometallate anions (VO₄³⁻, CrO₄²⁻, MnO₄⁻, V₁₀O₂₈⁶⁻, Cr₂O₇²⁻, Mo₇O₂₄⁶⁻, PW₁₂O₄₀³⁻ etc.),
- Anionic complexes of transition metals (Fe(CN)₆²⁻, [Ni(EDTA)]²⁻ etc.),
- Volatile organic anions (CH₃COO⁻, C₆H₅COO⁻, C₁₂H₂₅COO⁻, C₂O₄²⁻, C₆H₅SO₃⁻ etc.),
- Anionic polymers.

The presence of different types of anions in the interlayer spaces influences the distance between brucite-like layers, which may be described by parameter c of hydrotalcite unit cell or c'(c'=c/3). The values of some c' parameters characteristic for the presence of some inorganic anions in hydrotalcite structure are presented in Table 5.3 [185].

Table 5.3 Values of c' for some hydrotalcites (adapted from [185])

Anion	OH⁻	CO3 ²⁻	F	Cl	Br⁻	ľ	NO₃ ⁻	SO4 ²⁻	ClO₄ [−]
c' (Å)	7.55	7.65	7.66	7.86	7.95	8.16	8.79	8.58	9.20

It can be seen from Table 5.3 that in case of halides (monovalent) anions basal spacing increases with increasing anionic radius. On the other hand, the low distance reported for CO_3^{2-} (less than the CO_2 diameter) suggests a very strong interaction between layers and anions, which is caused by strong hydrogen bond in carbonate containing hydrotalcites. The low value of c' reported for OH^- is related to the strong hydrogen bridges between OH^- of the brucite-like layers and water. Therefore, the hydrotalcite-like materials with CO_3^{2-} and OH^- anions exhibit the best close-packed arrangement [185].

The type of anions present in the interlayer spaces determines chemical properties of hydrotalcite and availability of internal surface area for other species in chemical reaction. In general, organic anions are considered to favour ion-exchange, and thus it is easier to replace them in e.g. with anionic polymers. On the other hand, introduction of oxometallate anions or anionic complexes of transition metals allows to increase the composition of hydrotalcite by metals which cannot be introduced to brucite-like layers.

5.2 Properties

The physicochemical properties of hydrotalcite-like materials depend greatly on the chemical composition and preparation method of materials, i.e. morphology and texture of hydrotalcites is strongly influenced by the preparation method. Nevertheless, LDHs, due to their unique structure, exhibit some common features e.g. basic character or memory effect. One of the most important properties of hydrotalcite-like materials is the possibility of formation of homogenous mixtures containing well-dispersed elements in both layer and interlayer domains [188].

5.2.1 Thermal stability

Thermal stability of hydrotalcite-like materials is an important feature, as products of the thermal decomposition of LDHs find application in various branches of industry. Although hydrotalcite-like materials may differ greatly in the composition, they exhibit similar thermal decomposition behaviour [186]. The thermal decomposition of hydrotalcite materials usually is consisted of four consequent steps [193]: (i) removal of water physically adsorbed on the external surfaces of the crystallites (below 100°C), (ii) removal of interlayer water (up to 250°C), (iii) removal of hydroxyl groups from the layers as water vapour and (iv) decomposition of the interlayer anions (up to 500°C). The steps (iii) and (iv) usually overlap. Thermal treatment up to 500°C is associated with the loss of ca. 40 wt.% initial weight and has been reported for several hydrotalcite-like materials, which differed in composition [185, 189, 193-195]. As a result of thermal decomposition, the lamellar structure of hydrotalcites collapses and a new phase of periclase-like mixed nano-oxides is obtained [186].

Water and gaseous products of anion decomposition, upon release from hydrotalcite structure, may create channels in brucite-like layers, leading to the formation of additional porosity and mesoporous structure. Thus, mixed-oxides obtained during hydrotalcite calcination usually are characterized by higher specific surface area than the parental materials [185].

Upon further heating, the periclase-like structure of mixed oxides may undergo structural changes, leading to the formation of stable spinel phase. This phenomenon is dependent on material composition and usually takes place at high temperature (above 700°C). However, e.g. the formation of MgFe₂O₄ spinel was reported for Mg-Fe-CO₃ hydrotalcite already upon heating at 350° C [186].

5.2.2 Memory effect

Hydrotalcite-derived materials exhibit so-called 'memory effect', which consists of the ability to recover their original layered structure when mixed oxides, obtained upon thermal decomposition, are put in contact with a solution containing anions or an aqueous environment. Such effect is observed as long as starting hydrotalcite was calcined at moderate temperatures (usually below 550°C). Calcination at higher temperatures leads to the formation of stable spinel phase, and thus the material loses its ability to reconstruct layered structure [185-188].

The schematic representation of the reconstruction of lamellar structure by memory effect is presented in Fig. 5.3. As an example, thermal decomposition of Mg-Al-CO₃ hydrotalcite, followed by immersion in pure water (without contact to air) results in the formation of hydrotalcite-like structure with OH⁻ anions presented in the interlayer spaces known as meixnerite (Table 5.1).



Fig. 5.3 The simplified representation of the reconstruction of hydrotalcite structure – 'memory effect'

5.2.3 Acid-base properties

Hydrotalcites and hydrotalcite-derived materials are generally basic, as HTs possess basic surface hydroxyl groups. The basicity of the material depends strongly on the chemical composition of brucite-like layers, i.e. the nature and molar fraction of metal cations. The acidic-basic properties of hydrotalcites may be to some extent tailored e.g. by substitution of some cations by others with higher basicity, as for carbonate-containing hydrotalcites basicity is related to the electronegativity of the cations in brucite-like layers [188]. Another possibility, in which acid-base properties of HTs may be tailored, is the introduction of different species with acidic character into interlayers spaces.

The materials obtained upon hydrotalcite calcination show even more developed acidicbasic character. Typically, three types of basic sites may be distinguished on the surface of hydrotalcite-derived materials: (i) weak Brønsted basic sites – surface hydroxyl groups, (ii) intermediate-strength Lewis metal-oxygen pairs and (iii) strong basic sites – low coordinated O^{2-} anions, as confirmed by FTIR experiments of adsorbed CO_2 molecule [184, 196, 197] (Fig. 5.4). Additionally, acidic Mⁿ⁺ sites may also be distinguished.



Fig. 5.4 Adsorption of CO₂ on basic sites of hydrotalcite-derived material (adapted from [196, 197])

As reported in literature, the basicity of mixed oxides obtained by the thermal decomposition of hydrotalcites depends on the composition of the material precursor, i.e. layer composition [197-199], in case of catalysts the presence of additional species i.e. promoters [200] and the type of anions present in the interlayer spaces of hydrotalcites [201]. To mention an example, Tichit and Coq [184] reported that the replacement of Ni²⁺ by Mg²⁺ in Ni(Al)O hydrotalcite-derived oxide resulted in the decrease of the number of strong basic sites (O²⁻).

5.2.4 Anion Exchange Capacity

Hydrotalcites possess the ability of exchanging interlayer anions. This property is associated with non-divalent layer cation, and can be calculated as [186]:

$$ACE = \frac{x \, 10^5}{FW}$$
 (eq. 5.2)

where: FW – formula weight of hydrotalcite, x – amount of trivalent cations (x in eq. 5.1).

Anion exchange capacity of hydrotalcites is usually higher than that shown by cationic clays, and ranges between 200-400 cmol/kg. The values of ACE for selected hydrotalcite materials are presented in Table 5.4 [186].

Hydrotalcite [M ²⁺ -M ³⁺]-A ⁿ⁻	x	Formula weight (g/mol)	ACE (cmol/kg)
[Mg-Al]-CO₃	0.33	81.08	407
[Mg-Al]-NO ₃	0.33	91.64	360
[Mg-Al]-Cl	0.33	82.88	398
[Zn-Al]-Cl	0.33	110.41	299

Table 5.4 The values of anion-ecxchange capacity for selected hydrotalcites (adapted from [186])

The anion exchange properties depend strongly on the type of anion present in the interlayer spaces. E.g. carbonate-containing hydrotalcite exhibits strong interactions between CO_3^{2-} and brucite-like layers which results in close-packed arrangement, as discussed in Chapter 5.1 and

that is why it is difficult to exchange carbonate anions with others. In general, monovalent anions are more easily exchangeable than divalent anions.

5.3 Synthesis and modification of hydrotalcites

There is a number of different synthesis routes described in literature, which lead to hydrotalcite-like materials [185, 186, 188]. The most widely used are co-precipitation, urea, sol-gel or salt-oxide methods. The obtained materials can be further modified by anion exchange, reconstruction, microwave or hydrothermal treatments. The specification of desired hydrotalcite determines the selection of appropriate synthesis route.

5.3.1 Co-precipitation

The most common method of hydrotalcite preparation is co-precipitation, which involves the addition of a base to a solution containing a mixture of di- and tri-valent cations. The coprecipitation can be carried out at variable or constant pH. The former results first in the formation of hydroxides or hydrous oxides, and only further addition of base results in the co-precipitation or conversion to hydrotalcite structure. The latter is recommended when hydrotalcite-like material with high chemical homogeneity is required. pH is kept constant by simultaneous addition of a base and a mixed salt solution. The co-precipitation method may be demonstrated by equation [186]:

 $(1-x)M^{2+}A_{2/n}{}^{n-} + xM^{3+}X_{3/n}{}^{n-} + 2NaOH + mH_2O \rightarrow [M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2][(A^{n-}{}_{x/n})\cdot mH_2O] + 2NaA^{n-}{}_{1/n} (eq. 5.3)$

The selection of appropriate pH for co-precipitation is a crucial parameter, which may influence chemical, structural and textural properties of the resulting material. Moreover, coprecipitation may be influenced by competitive reactions depending on the pH and nature of desired hydrotalcite composition, such as precipitation of separate phases of metal hydroxides or precipitation of metal salts in case of oxoanions with high metal ion affinity. Thus, co-precipitation method may be sometimes limited. However, it gives an opportunity to synthesize a wide range of hydrotalcite-like materials with halides, nitrate or carbonate anions in the interlayer spaces, which may be further modified by ion-exchange, reconstruction or hydrothermal treatment in order to modify material composition and structure [185].

The co-precipitation method has been proven to give hydrotalcite-like materials which exhibit high crystallinity, small particle size, high specific surface area and high average pore diameter, making these materials suitable for industrial applications [186].

5.3.2 Urea method

An alternative to synthesis via co-precipitation is urea method. Upon co-precipitation, the supersaturation of the precipitating agent, i.e. OH⁻, is reached rapidly, which results in continuous nucleation of mixed hydroxides and aggregation of the particles. Thus, synthesized hydrotalcite is characterized by a wide particle size distribution [186]. On the other hand, in case of urea method, the precipitating agent is retardant, leading to the separation of the nucleation and aggregation processes, and thus monodisperse particles are obtained [202-204]. Urea is a very weak Brønsted base, highly soluble in water, which undergoes hydrolysis producing in this way in-situ OH⁻ ions, according to the reactions presented on Fig. 5.5 [204]. The hydrolysis rate of urea can be strongly controlled by temperature, which thus allows to control co-precipitation process.



Fig. 5.5 The scheme of the decomposition of urea in aqueous solution (adapted from [204])

The urea method was reported to give hydrotalcite-like materials with very high crystallinity, large crystallites (in the range of μ m) and very homogenous particle size. The method was also reported to be suitable for obtaining hydrotalcites with hexagonal shape [186].

5.3.3 Sol-Gel method

The sol-gel method involves in the first step the formation of a mobile colloidal suspension (sol), which is subsequently gelling through internal cross-linking. The hydrotalcite-like materials are formed through hydrolysis and subsequent condensation of a solution which typically contains alkoxides and/or acetylacetonates [188]. The materials prepared by sol-gel method exhibit higher thermal stability (up to 550°C), higher specific surface area due to the increase in mesopore volume with respect to co-precipitated samples. On the other hand, co-precipitation results in the formation of materials with higher crystallinity. It has been also reported that sol-gel technique may result in the materials with increased basicity due to the difference in texture and morphology of prepared hydrotalcites [186].

5.3.4 Salt-oxide method (Induced Hydrolysis)

Salt oxide method involves a reaction between metal oxide, such as MgO, ZnO or CuO and metal salts, typically nitrates or chlorides, such as AlCl₃, CrCl₃. Metal oxides are progressively dissolved, resulting in co-precipitation of hydrotalcite-like materials. This process can be expressed by reaction 5.4 [186, 188]:

$$M^{2+}O + xM^{3+}A^{n-}_{3/n} + (m+1)H_2O \rightarrow [M^{2+}_{1-x}M^{3+}_x(OH)_2][(A^{n-}_{x/n})\cdot mH_2O] + 2M^{2+}A^{n-}_{2/n}$$
(eq. 5.4)

The salt-oxide method may be also applied to reactions between divalent-divalent, divalent-trivalent and trivalent-trivalent species [186].

5.3.5 Reconstruction

Reconstruction method can be considered as one of the techniques useful to modify hydrotalcite structure. It utilizes the fact that hydrotalcite-like materials exhibit the possibility of reconstructing its layered structure after calcination at moderate temperatures (memory effect – Chapter 5.2.2). In this way hydrotalcite structure can be intercalated with various type of anions e.g. $CrO_4^{2^-}$, $HPO_4^{2^-}$, $SiO_3^{2^-}$, $HGaO_3^{2^-}$ or large organic anions [186].

The calcination conditions (temperature, rate, duration) influence material ability to reconstruct its structure. High temperatures (above 550°C) may result in the formation of stable spinel phases, and thus make it impossible for mixed-oxide to reorganize to hydrotalcite structure. Moreover, the conditions of reconstruction also influence the structure and composition of reconstructed hydrotalcite. Typically, reconstruction is carried out by 24h-rehydration of mixed oxide powder in an aqueous solution containing appropriate anions. This process should be performed in the inert environment in order to avoid contamination by carbonate anions, as CO₂ exhibits high affinity to brucite-like layers and is soluble in water.

The reconstruction technique has its limitations. It has been reported that repeated calcination/rehydration cycles result in the decrease of the content of interlayer carbonate anions and an increase in the extraction of AI^{3+} from brucite-like layers. Moreover, not all $M^{2+}-M^{3+}$ combinations can undergo reconstruction. E.g. the reconstruction of Fe³⁺ hydrotalcites is limited due to the formation of MgFe₂O₄ spinel phase upon calcination even at low temperatures [186].

5.3.6 Anion-exchange

Another possibility of modifying hydrotalcite structure and obtaining a material with a new chemical composition is ion-exchange method, which makes use of high anion exchange

capacity of hydrotalcite. Anion exchange in hydrotalcite-like materials depends mainly on the electrostatic interactions between positively charged brucite-like layers and the exchanging anions. It has been reported that equilibrium constants of exchange increase with the decrease of the anion radii. Thus, anion exchange is favoured for ingoing anions with a high charge density [186]. Basing on thermodynamic calculations and experimental results, a certain sequences of anions affinity to hydrotalcite structure have been established (Table 5.5) [186].

The orders presented in Table 5.5 prove a very strong affinity of carbonate anions to hydrotalcite structure. Therefore, similarly as in the reconstruction method, it is important to carry out anion exchange under CO₂-free atmosphere. It can be also seen that in general the affinity for divalent anions is higher than for monovalent anions. Thus, the best precursors for anion exchange modification are nitrate- and chloride-containing hydrotalcites [185, 186].

 Table 5.5 The order of affinity of different anions to hydrotalcite [186]

5.3.7 Hydrothermal treatment

Textural and structural properties of synthesized hydrotalcites may be controlled by the application of different post-synthesis treatments. Most commonly used procedure is hydrothermal treatment, which involves aging of hydrotalcite mineral suspension at desired temperatures and pressures. Hydrothermal treatment is aimed at improving appropriate material crystallinity or anion-exchange properties. However, this procedure strongly influences the chemical composition of the material e.g. M²⁺/M³⁺ molar ratio, as the treatment may result in a partial leaching of cations from brucite-like layers [186, 188].

Similarly, microwave or ultrasound treatments were also reported as modification techniques, resulting in the increased crystallinity of hydrotalcite-like materials [205, 206].

5.4 Applications of hydrotalcite-like materials

Hydrotalcite-like materials and products of their thermal decomposition have found very broad applications in various fields thanks to their exceptional properties. Current applications of hydrotalcite materials are shown in Fig. 5.6. The following subchapter is focused mostly on applications of HTs and its derivatives in catalysis and as CO₂ adsorbents.



Fig. 5.6 Some applications of hydrotalcite-like materials

5.4.1 Adsorption of CO₂

Because of their basic character hydrotalcites have been studied as potential adsorbents of CO₂. Special attention has been paid to its application as adsorbents in separation of CO₂ from flue gases in fossil fuel-based power plants [207, 208] or in in-situ separation of CO₂ from reaction chambers [209-211], so called sorption-enhanced reaction processes (SERP), where carbon dioxide is considered as a by-product. The former offers benefits of in-plant utilization of CO₂ as a feedstock for further catalytic processes, e.g. dry reforming of methane. SERP can be used in steam reforming of methane technology, resulting in the increase of hydrogen production by shifting equilibrium according to Le Chatelier's principle, and in higher H₂ purity [211, 212]. Both concepts contribute to carbon dioxide mitigation and address the problem of CO₂ emissions.

 CO_2 adsorption capacity on hydrotalcites depends on several factors, such as temperature of adsorption, M^{2+}/M^{3+} molar ratio, type of cations in brucite-like layers, type of anions in the

interlayer spaces, the water content/presence of steam and the presence of promoters [210, 212]. Adsorption capacities of various hydrotalcites reported in literature is presented are Table 5.6.

Hydrotalcite	T _{ads} (°C)	P _{tot} (bar)	Gas composition	Sorption capacity (wt.% of CO ₂)
MgAI-HT	200	1	100% CO ₂	3.7
MgAI-HT	350	13	53% CO ₂	7.0
K-promoted MgAl-HT	208	-	20% CO ₂ , 30.5% H ₂ O, He	4.0
Cs-promoted MgAl-HT	403	2	20% CO ₂ , 26.5% H ₂ O, He	3.3
NiMg-HT	20	1	100% CO ₂	6.9

Table 5.6 CO₂ adsorption capacities of main HTs reported in literature (adapted from [212])

Cations in brucite-like layers possess different basicities, and thus the affinity of CO_2 towards them also differs. Yong et al. [210] reported that at 25°C adsorption of CO_2 on different hydrotalcites decreased in the order: NiAl > MgAl > CoAl > ZnAl > CuAl, while at 300°C the highest adsorption capacity was exhibited by CoAl hydrotalcite. The M^{2+}/M^{3+} may also modify CO_2 adsorption capacities of HTs. E.g. in case of Al³⁺-containing hydrotalcites, the density of the layer charge increases with increasing content of alumina, which favours adsorption of CO_2 . On the other hand, with the increasing alumina content, the decrease in the interlayer spacing is observed, which results in decrease of high strength carbon dioxide adsorption sites. Similarly, the presence of different types of anions influences the basal spacing between hydrotalcite layers, and thus its adsorption capacities for alkali metals (K, Cs) promoted hydrotalcites.

The presence of water or steam was proven to increase CO₂ adsorption capacity of HTs [207, 210-212]. H₂O may have double effect on CO₂ adsorption of hydrotalcites [210]: (i) increase potential energy and (ii) activate adsorption sites by maintaining the hydroxyl concentration of the surface, and preventing site poisoning by carbonates or coke deposition. Moreover, as reported by Ding et al. [207], purging adsorbent with steam facilitates recovery of CO₂.

Hydrotalcites have different thermal decomposition behaviours depending on the chemical composition, thus the CO_2 adsorption capacity can differ for different materials with the increase in temperature.

In contrast to other materials tested for CO_2 adsorption, such as carbonaceous materials, zeolites, metal organic frameworks, amine sorbents, carbonates or silica, hydrotalcite-like materials show good stability in the presence of water and in cyclic operation [212].

5.4.2 Catalysis

The application of hydrotalcites and hydrotalcite-derived materials in catalysis is connected mainly to their basic properties, and thus they may be treated as a solid base catalysts. Additionally, there is a possibility of introducing new active sites, e.g. redox centres into hydrotalcite structure by various modifications, such as reconstruction or anion exchange. Moreover, they possess a number of characteristics desired in a catalyst, among others high specific surface area (between 100-300m²/g). The materials after calcination, even at high temperatures, are very homogenous and exhibit high dispersion of metal species that may show synergetic effect in catalysis process. Reduced metal species on the catalyst surface show excellent anti-sintering properties, due to the confinement of the lamellar structure and strong-metal support interactions. Finally, the synthesis of hydrotalcite-like materials is quite simple and may be strongly controlled, which gives an opportunity to tailor desired composition and desired properties of the catalyst.

Hydrotalcite-derived materials as base catalyst found application in a number of processes, mainly in organic chemistry, such as aldolization of acetone, Michael additions reactions, aldol condensation etc (Table 5.7) [184].





Cations in HT structure	Preparation method of hydrotalcite precursor	Reaction/Process	Ref.
NiMgAl	Co-precipitation	Partial Oxidation of Methane	[213, 214]
NiMgAl	Co-precipitation	Partial oxidation of methane, and steam reforming of methane	[215]
NiMgAl, RhMgAl	Co-precipitation	Partial oxidation of methane, and steam reforming of methane	[216]
NiAl, CoAl, NiAlSn, CoAlSn	Co-precipitation	Decomposition of methanol, PO of methanol, SR of methanol, oxidative SR of methanol	[217]
NiAl	Co-precipitation	Steam reforming of methanol	[218]
CuZnAl(Zr)	Co-precipitation	Oxidative steam reforming of methanol	[219]
La, Ce promoted NiMgAl	Co-precipitation followed by anion exchange	Ethanol steam reforming	[220]
Ce and Pr-promoted NiCoMgAl	Co-precipitation followed by anion exchange	Ethanol steam reforming	[221]
NiZnAl, CuZnAl	Co-precipitation	Water Gas shift	[222]
Pt, Ru, Rh-promoted CuZnAl	Co-precipitation followed by regeneration	Water Gas Shift	[223]
CoMgAl, CuMgAl, CuCoMgAl	Co-precipitation	Selective Catalytic Reduction of NO by ammonia	[224]
MgCuFe	Co-precipitation	Selective Catalytic oxidation of ammonia to nitrogen	[225]
MgZnAlFe	Co-precipitation	NO _x storage/reduction	[226]
CuMgAl, CoMgAl, CuCoMgAl, NiMgAl, MgFeAl	Co-precipitation	N ₂ O decomposition	[227]
CuMgAl, CoMgAl, CuCoMgAl	Co-precipitation	Oxidation of mono-carbon Volatile Organic Compounds (VOC)	[228]
MgFeCr	Co-precipitation	Catalytic Reduction of N₂O by ethylbenzene	[229]
MgAl	Co-precipitation	Aldol condensation of citral and acetone	[230]
CuMgAl	Co-precipitation	Hydroxylation of phenol	[189]
FeMgAl, CuMgAl, NiMgAl, CoMgAl	Co-precipitation	Ozonation of phenol and oxalic acid	[231]
MgFeAl	Co-precipitation	Transestrification of soybean oil with methanol	[232]

 Table 5.7 Hydrotalcite-derived catalysts used in various catalytic processes reported in literature

Another possibility is to apply hydrotalcites as precursors of supported metal catalysts, which possess metal as well as acidic and basic sites. In general, there are three main routes leading to supported metal catalysts derived from hydrotalcites, shown schematically in Fig. 5.7. The first one involves synthesis of hydrotalcite precursor with desired metal cations in brucite-like layers. In

the second route, initial hydrotalcite undergoes ion exchange with anionic metal precursor containing desired metal. Third route involves the deposition of inorganic or organometallic precursors of metals on the calcined hydrotalcite material and the subsequent reconstruction of hydrotalcite structure. All preparation routes in the final stage involve calcination and/or reduction resulting in the final supported metal catalyst.

A summary of various catalytic processes which applied hydrotalcite-derived catalysts is presented in Table 5.7. The supported metal catalysts obtained from HTs precursors have been proven to be effective in environmental processes, such as partial oxidation of methane and methanol, steam reforming of methane, methanol and ethanol, oxidative steam reforming of methanol, water gas shift reaction, selective catalytic reduction of NO, selective catalytic oxidation of NH₃, NO_x storage/reduction, N₂O decomposition and oxidation of VOCs. Hydrotalcite-derived catalysts containing nickel have been also widely studied in dry reforming of methane, which is described in detail in the next subchapter.

5.5 Hydrotalcites in DRM

As reported in Chapter 4, the promising catalysts for dry reforming reaction are nickelbased ones supported on mixed magnesia-alumina. These supports guarantee intermediatestrength interactions between nickel active sites and their carrier, preventing in this way sintering of active material and the formation of inactive phases (NiAl₂O₄ or NiO-MgO solid solution). Moreover, the industrial processes which apply DRM reaction combined with SRM are based on similar catalytic systems. Thus, hydrotalcite-like materials seem to be very promising catalysts precursors for DRM reaction, as it is possible to design material composed of Ni, MgO and Al₂O₃ with very good homogeneity. Additionally, by precursor modification via anion exchange or reconstruction methods it is possible to introduce various promoters into catalytic system. The following chapter summarizes the studies on catalytic performance of nickel-based hydrotalcitederived materials in the DRM reaction reported so far in literature.

5.5.1 Ni/Mg/Al and Ni/Al hydrotalcite-derived catalysts

The substitution of a part or all of Mg²⁺ cations by Ni²⁺ in the Mg,Al-CO₃ hydrotalcite structure results in the simplest catalytic systems which can be applied in dry reforming reaction. The materials based on Ni/Mg/Al and Ni/Al hydrotalcites tested in DRM and reported in literature are presented in Table 5.8.

Bhattacharyya et al. [118], as one of the first, tested hydrotalcite-derived Ni/Al and Ni/Mg/Al mixed oxides catalysts in the combined dry/steam reforming reactions and compared

their catalytic activity to the commercial NiO supported catalysts. Their studies showed that both Ni/Al and Ni/Mg/Al catalysts exhibit very good activity at the similar level to the commercial material. Hydrotalcite-derived samples turned out to be more active under more severe reaction conditions (higher GHSV, and lower H₂O/CH₄ feed gas composition) and more resistant to coke formation, indicating that the hydrotalcite-derived catalysts are promising materials for dry reforming reaction. This research was continued by several researchers and the comparison of Ni/Al and Ni/Mg/Al hydrotalcite-derived materials tested in dry reforming reaction is summarized in Table 5.8.

Shishido et al. [119] compared catalytic activity of Ni/Mg/Al hydrotalcite-derived catalyst synthesized via co-precipitation method and 25.1 wt% Ni impregnated on Mg/Al hydrotalcite-derived catalyst with conventional Ni/MgO and Ni/Al₂O₃ catalysts. Hydrotalcite-derived materials showed higher conversions of both CO₂ and CH₄. The co-precipitated sample exhibited the highest catalytic activity at 800°C, which was explained by the formation of highly dispersed and stable nickel species on the catalyst surface.

The influence of Mg/Al molar ratio in Ni/Mg/Al hydrotalcites was examined by Zhu et al. [120]. The authors varied Mg/Al molar ratio from 1/5 to 5. The results of catalytic tests showed that the performance of hydrotalcite-derived materials was dependent on the Mg/Al molar ratio, and was increasing with increasing Mg/Al, pointing to the strong influence of magnesia content on the DRM reaction. Moreover, the sample with the highest magnesium content exhibited also the highest resistance to coke formation. However, it is important to stress, that high Mg/Al ratios resulted in the formation, beside hydrotalcite structure, of Mg₅(CO₃)₄(OH)₂·3H₂O phase, thus catalytic activity of the sample with the highest Mg/Al ratio may have been affected by the presence of MgO phase.

Touahra et al. [121] studied hydrotalcite derived Ni/Al mixed oxides with varying Ni/Al molar ratio (2, 3, 5, 8, 10) in DRM in the temperature range of 400-700°C. The samples calcined at 800°C exhibited the presence of NiAl₂O₄ spinel phase, which was explained as the main reason for the high stability of the catalysts tested in DRM. The best catalytic performance was shown by NiAl-HT sample with Ni/Al ratio equal to 2, pointing to the influence of Ni/Al molar ratio on the Ni particle size, and stability of the material. Thouahra et al. [121] examined also the influence of calcination temperature on the performance of Ni/Al catalysts showing that temperature below 500°C is not affecting the catalytic activity.

)												
	Method of	Cations in	Ni/Mg			Re	action c	onditions		Conver	sion ²⁾	H ₂ /	
catalyst	hydrotalcite synthesis	HTs layers	or NI loading ¹⁾	M ²⁺ /M ³⁺	conditions	Temp. (°C)	CH₄/ CO₂	GHSV (h ⁻¹)	TOS (h)	CH₄ (%)	CO ₂ (%)	C (C	Ref.
NiAl and NiMgAl HTs	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1, 0.2	2, 3	pu	815	1.25	720	250	70	52	1.0	[118]
NiMgAl HTs; Ni supported on	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1/2	n	650 and 850°C for	800	$1/1^{3)}$	54000	9	94	pu	pu	[119]
MgAI HT	Impregnation of Ni ²⁺ on MgAl HT	Mg ²⁺ , Al ³⁺	25.1 ¹⁾	ſ	14h in air					92	pu	pu	
NiMgAl HTs	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1/5, 1/3, 1	6, 4, 2, 2/3,2/5	500°C for 10h in air	800	1/1	80000	30	82	88	pu	[120]
NIAI HTS	Co-precipitation at constant pH	Ni ²⁺ , Al ³⁺	I	2, 3, 5, 8, 10	300, 400, 500, 600, 700, 800°C for 6h	700	1/1 ³⁾	pu	10	88	88	1.0	[121]
NiMgAl HTs	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	0.5, 1, 2, 5	0.4, 0.9, 2	400, 600, 800°C for 6h in air	650	1/2 ³⁾	45000 ⁴⁾	pu	83	38	1.2	[122]
Ni supported on MgAl HTs	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1, 3, 5, 10, 15 ¹⁾	pu	900°C for 5h	750	1/1	50000	10	85	96	0.9	[123]
NiMgAl HTs	Sol-gel method	Ni ²⁺ , Mg ²⁺ , Al ³⁺	4, 15, 19 ¹⁾	pu	500, 650°C for 5h	800	$1/1^{3)}$	2.94 10 ^{-5,5)}	∞	96	94	pu	[124]

Table 5.8 The summary of Ni/Mg/Al and Ni/Al hydrotalcite-based catalytic systems tested in dry reforming of methane

Chapter 5. Hydrotalcites
Type of	Method of	Cations	Ni/Mg or Ni		Calcination	Re	action c	conditions		Conver	sion ²⁾	H ₂ /	
catalyst	hydrotalcite synthesis	in HTs layers	loading ¹⁾	M ²⁺ /M ³⁺	Conditions	Temp. (°C)	CH₄/ CO₂	GHSV (h¹)	TOS (h)	CH₄ (%)	cO ₂ (%)	(-)	Ref.
NiMgAl HTs	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	3, 6, 9, 12, 15,18 ¹⁾	ß	800°C for 5h	600	$1/1^{3)}$	6000	25	41	50	0.7	[125]
Ni introduced into MgAl HTs	Co-precipitation in [Ni(EDTA)] ²⁻	Mg ²⁺ , Al ³⁺	ı	ſ	500°C for 16h in air	800	$1/1^{3)}$	ри	150	98	95	1.0	[126]
	Co-precipitation in [Ni(EDTA)] ²⁻	Mg ²⁺ , Al ³⁺	1/7	3.5						67	95	1.0	[127]
Ni introduced	Anion exchange	Mg ²⁺ , Al ³⁺	1/11	3.3	500°C for	800	$1/1^{3)}$	pu	9	97	95	1.0	
into MgAl HTs	Reconstruction	Mg ²⁺ , Al ³⁺	1/11	3.6	16h in air				1	97	94	1.0	
	Co-precipitation	Mg ²⁺ , Al ³⁺	1/5	2.5						98	96	1.0	
NiMgAl HTs	Surfactant- assisted co- precipitation	Ni ²⁺ , Mg ²⁺ , Al ³⁺	10 ¹⁾	ſ	700°C for 6h	800	1/1	6000	35	47	62	pu	[128]
NiMgAI HT	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	2.94	2	350, 600, 800, 1000°C	006	32/ 40 ³⁾	ри	10	74	pu	pu	[131, 132]
NiMgAI HT	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1/6	2.45	700, 900°C for 14h	750	1/1	ри	pu	29	50	pu	[134]

Table 5.8 continuation

	Method of	Cations	Ni/Mg		Calcination	Re	action c	ondition	S	Conver	sion ²⁾	$H_2/$	
Type of catalyst	hydrotalcite synthesis	in HTs layers	or N loading ¹⁾	M ²⁺ /M ³⁺	conditions	Temp. (°C)	CH₄/ CO₂	GHSV (h ⁻¹)	TOS (h)	CH₄ (%)	CO ₂ (%)	CO (-)	Ref.
NiMgAl and	Co-precipitation	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1.125	2	800°C for 6h	750	1/1 ³⁾	300	×	93	95	1.0	[133]
NIAl HTS	at constant pH	Ni ²⁺ , Al ³⁺	I	2	in air		Ĩ	000	1	68	06	0.7	
NiMgAl HTs	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	10 ¹⁾	1.5-9	800°C for 3h	800	1/1	ри	4	86	87	pu	[129]
NiMgAl HTs	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	10 ¹⁾	m	500-800°C for 6h	800	1/1	8000	2000	92	95	6.0	[130]
	Sol-gel method	Ni ²⁺ , Mg ²⁺ , Al ³⁺	4 E 1)	0.25-19	750°C for 5h		1 (1 3)		ç	84	89	pu	[103]
	Co-precipitation at constant pH	Ni ²⁺ , Mg ²⁺ , Al ³⁺	CT	2	in air	000	. т / т	000005	5 0	84	89	pu	
¹⁾ weight % of Ni load ²⁾ results obtained for	ling; r the best catalyst;												
^{ع)} gases were diluted ⁴⁾ WHSV (cm ³ /h/g _{cat}); 5) M /E (مها رحm ³)	with inert gas;												
nd -no data													

Table 5.8 continuation

On the other hand, temperatures above 500°C could modify catalytic properties of the samples due to the formation of spinel phases, which increased interactions between the support and active material. Similar results were obtained by Perez-Lopez et al. [122] who studied the effect of composition and calcination temperature of Ni/Mg/Al hydrotalcite-derived catalysts with varying M^{II}/M^{III} and Ni/Mg molar ratios on their catalytic activity in DRM reaction. They observed that catalytic performance of Ni/Mg/Al hydrotalcites was mostly affected by M^{II}/M^{III} molar ratio rather than Ni/Mg ratio, being the most efficient for catalysts with Ni/Mg ratio between 1-5 and fixed M^{II}/M^{III} ratio around 2, calcined at 600°C and reduced at 700°C.

Nickel supported on MgAl₂O₄ spinels obtained from Mg/Al hydrotalcite precursor by calcination at 800°C were studied by Guo et al. [123] and their performance was compared to Ni/γ-Al₂O₃ and Ni/MgO-Al₂O₃. The results showed that Ni supported on MgAl₂O₄ was a highly active catalytic system with good stability due to the interactions between active phase and support. The Ni/MgAl₂O₄ system gave catalysts with high dispersion of nickel species which was responsible both for high activity and resistance to coking and sintering. Though the 55h-test at 750°C over 5%Ni/MgAl₂O₄ resulted in the formation of two types of coke deposits on the catalysts surface, the carbon deposits were not poisonous to the catalyst and did not affect CH₄ and CO₂ conversions.

Gonzalez et al. [124] studied Ni/Mg/Al hydrotalcite-derived mixed oxides with 4, 15 and 19wt.% of nickel prepared by sol-gel method. They also checked the influence of moderate calcination temperatures (500-650°C) in order to avoid the formation of spinel structures. The prepared catalysts were affected by side reactions CH₄ decomposition, Boudouard reaction and RWGS. The best catalytic performance was shown by the catalyst with 15% nickel loading, calcined at 650°C, as it gave high conversions of CH₄ and CO₂ and, at the same time, produced the lowest amounts of carbon and H₂O. The amount of carbon formed during reaction was influenced by the calcination temperature of hydrotalcite precursor and was decreasing with increase in temperature.

The effect of nickel loading within the range of 3-18 wt.% for Ni/Mg/Al hydrotalcite derived mixed oxides was investigated by Lin et. al. [125]. The authors found that both CH₄ and CO₂ conversions increased with increasing Ni loading. However, the influence of side reactions, namely CH₄ decomposition and CO disproportionation, was more evident at low temperatures for the catalysts with high nickel content. The 30h tests carried out at 600 and 750°C showed that the stability of the catalysts was dependent on reaction temperature and nickel content. At 750°C it was increasing with increasing nickel content. The opposite trend was observed at 600°C. The coke deposition over the catalysts tested at 600°C was increasing with Ni loading, as a result of the

sintering of nickel particles, and thus promotion of carbon-forming reactions. On the other hand, at 750°C the amount of coke deposits was decreasing with increasing Ni content.

Tsyganok et al. [126] proposed a new method of Ni introduction into hydrotalcite structure by co-precipitation of Mg/Al hydrotalcite in the solution of stable [Ni(EDTA)]²⁻ chelates. The so-prepared materials showed the presence of nickel-EDTA species in the interlayer spaces of hydrotalcites. The catalyst showed a stable performance during 150h stability tests at 800°C. Different forms of coke deposits were present on the catalysts surface after the reaction, pointing to the occurrence of carbon forming reactions (CH₄ decomposition and Boudouard reaction). However, it did not affect catalysts activity. Nickel-containing Mg/Al-derived hydrotalcites exhibited higher conversions of CO₂ than methane, indicating the occurrence of RWGS reaction, which affects products distribution. Another study carried out by Tsyganok et al. [127] involved the comparison of catalytic performance in DRM reaction of Mg/Al hydrotalcite-derived catalysts into which nickel species were introduced via different preparation techniques, such as: co-precipitation of Mg²⁺ and Al^{3+} with pre-synthesized [Ni(EDTA)]²⁻ complexes; anion exchange reaction of NO₃²⁻ ions present in the hydrotalcite interlayer spaces with [Ni(EDTA)]²⁻ chelate in aqueous solution; calcination of Mg/Al hydrotalcite at moderate temperature, followed by reconstruction of hydrotalcite layered structure in an aqueous solution of [Ni(EDTA)]²⁻; and traditional co-precipitation of Ni²⁺, Mg²⁺ and Al³⁺ with CO₃²⁻. All prepared catalysts showed stable performance and high conversions of both CH₄ and CO₂.

Tan et al. [128] studied Ni/Mg/Al mixed oxides derived from hydrotalcites, which were synthesized via surfactant-assisted co-precipitation method. The authors used 3 different surfactants at the co-precipitation stage in order to modify catalysts properties (texture, reducibility, structure and nickel distribution on the catalysts surface). The DRM catalytic tests showed that the surfactants significantly affected the catalytic performance of materials, especially the co-precipitation in the presence of tetrapropylammonium hydroxide (TPAOH) resulted in the increase of CH₄ and CO₂ conversions. The charge properties and coordination abilities towards metal ions of different surfactants may influence the growth of specific crystal planes. The authors showed that the catalytic performance in DRM reaction was strongly affected by the exposure of Ni(200) plane. The improved catalytic performance of the sample synthesized in the presence of TPAOH was explained by the increase in the exposure of Ni(200) plane. Nevertheless, all tested catalysts showed a decrease in catalytic activity at 800°C over 40h tests.

5.5.2 Ce promotion

The addition of cerium to Ni/Mg/Al hydrotalcites was widely studied by Daza et al., who investigated the effect of the method of cerium introduction [233], of Ce loading [234-236] and hydrotalcite preparation method [237]. The authors compared DRM catalytic performance of Ni/Mg/Al co-precipitated material with Ce-promoted samples (5 wt.% of Ce) prepared via co-precipitation in solutions of Na₂CO₃, [Ni(EDTA)]²⁻ and [Ce(EDTA)]⁻ [233]. In all cases, ceria-promoted samples exhibited higher activity than unpromoted catalyst. The promoting effect of ceria was attributed to the increase of reducibility of nickel species without simultaneous reduction in the size of the formed Ni particles. The best catalytic performance was observed for the catalyst obtained by conventional co-precipitation in Na₂CO₃, with average CH₄ and CO₂ conversions after 200h TOS equal to ca. 78% and 87%, respectively. Moreover, it was observed that the sample loaded with a small amount of Ni (prepared via co-precipitation in solution of [Ni(EDTA)]²⁻ complexes) exhibited similar performance to the samples loaded with much higher Ni content, which was attributed to the formation of very small nickel crystallites (smaller than 5nm).

Daza et al. [234] also studied the influence of Ce content in Ni/Mg/Al hydrotalcite-derived catalysts. Ceria was introduced into hydrotalcite structure by reconstruction method with [Ce(EDTA)]⁻ complexes and nominal loading of Ce was equal to 0, 1, 3, 5 or 10 wt.%. Ce-promoted materials exhibited an increase in total basicity after calcination and reduction in the stream of H₂ with the increasing ceria content. The authors confirmed the coexistence of Ce₂O₃ and CeO₂ on the catalyst surface. CO₂ during DRM may be adsorbed on the redox centres of Ce₂O₃, producing CO and CeO₂ in a redox cycle. CeO₂ may further react with deposited carbon, giving Ce₂O₃ and CO₂. This proposed mechanism may explain the increase in total basicity and the increased stability of Cepromoted catalysts. In general, higher conversions of CH₄ than CO₂ were observed for ceria containing samples, which may be explained by the conversion of methane into light hydrocarbons or by the CH₄ decomposition. The amount of Ce introduced did not have significant influence on CH_4 and CO_2 conversions and H_2/CO molar ratio. However, it influenced the formation of carbon deposits. The smallest amounts of catalytic coke were formed on the samples loaded with small amount of Ce, between 1-3 wt.%. Thus, the authors stated that the optimal nominal value of Ce promotion is 3 wt.% [235]. Similar conclusions were driven in another study of these authors, where ceria was introduced into hydrotalcite catalytic system at the co-precipitation stage and samples with different Al/Ce molar ratios were studied [236]. The reducibility of the catalysts was increasing with the increasing ceria content, i.e. decreasing Al/Ce ratios, which resulted in the formation of bigger Ni crystallites, and thus had negative effect on the catalysts stability.

The same authors also compared the performance of Ni/Mg/Al hydrotalcites synthesized via co-precipitation and self-combustion in glycine methods [237]. Mixed oxides obtained by calcination of resulting hydrotalcites underwent additionally reconstruction in solution of [Ce(EDTA)]⁻ complexes. Much better performance was shown by the sample derived from self-combusted hydrotalcite, and this catalyst exhibited higher value of specific surface area, pore volumes and total basicity.

Method of hydrotalcite synthesis	Method of Ce introduction into HT structure	Ni/ Mg	Ce content (wt.%)	Calcination conditions	Ref.
Co-precipitation in solution of Na ₂ CO ₃ , [Ce(EDTA)] ⁻ or [Ni(EDTA)] ²⁻	At co-precipitation stage in form of Ce ³⁺ cations or [Ce(EDTA)] ⁻	1/2	5	500°C for 16h in air	[233]
Co-precipitation at constant pH	Reconstruction method with solution of [Ce(EDTA)] ⁻	2	0, 1, 3, 5, 10	500°C for 16h in air	[234]
Co-precipitation at constant pH	Reconstruction method with solution of [Ce(EDTA)] ⁻	2	0, 1, 3, 10	500°C for 16h in air	[235]
Co-precipitation at constant pH	At co-precipiatation stage in form of Ce ³⁺ cations	2	24, 9, 4, 1,5 ¹⁾	500°C for 16h in air	[236]
Co-precipitation at constant pH and self- combustion method	Reconstruction method with solution of [Ce(EDTA)] ⁻	2	3	500°C for 16h in air	[237]
Co-precipitation at constant pH	At co-precipitation stage in form of Ce ³⁺ cations and by impregnation	20 ²⁾	1-10 ¹⁾	500°C for 4h	[238]

Table 5.9 Methods of ceria introduction into Ni/Mg/Al hydrotalcite derived mixed oxides tested in DRM

¹⁾ Al/Ce molar ratio

²⁾ weight % of Ni

Recently, Ni/Mg/Al promoted hydrotalcites were also studied by Ren et al. [238], who investigated DRM reaction at high pressure (0.5 MPa). The results confirmed anti-coking benefits of ceria addition. However, the effect of Ce-promotion depended on the amount and the method of ceria introduction. The Ce-impregnated samples were more effective in the inhibition of coke deposits formation than co-precipitated ones, which was explained by the higher content of Ce³⁺ on the catalyst surface and more lattice defects of CeO₂ in case of the former samples. The samples were very active in pressurized DRM reaction and showed initial CH₄ conversion at 750°C close to equilibrium limit. However, carbon deposition was observed over catalyst surface. The deactivation of catalyst followed the sequence of ceria content and was increasing with the increase of Ce

loading. These results are in agreement with those reported by Daza et al. [234], that high additions of ceria may have negative effect on catalyst stability due to enhanced reducibility of nickel species, and thus formation of bigger crystallites on catalyst surface.

The comparison of different methods of ceria introduction into Ni/Mg/Al hydrotalcitederived mixed oxides reported in literature is presented in Table 5.9.

5.5.3 Other promoters

The effect of various promoters, other than cerium, on the performance of NiMgAl hydrotalcite-derived catalysts is presented in Table 5.10.

Promoter	Catalyst	Promoter loading (wt.%)/Method ¹⁾	Effect of addition	Ref.
La	NiMgAl-HT	0, 0.04, 0.11, 0.18 ²⁾ /CP	Increased stability and activity	[239]
La	NiMgAl-HT	1.1, 2/CP	Increased stability and decreased activity	[240 <i>,</i> 241]
La	10 wt.% Ni	10/IMP	Increased reducibility of Ni;	
Rh	impregnated on MgAl-HT	1/IMP	Promotes carbon formation	[242]
CeZrO ₂	NiMoMgAl-HT	0, 5, 10, 15, 20/CP	Increased catalyst activity; Promotes reducibility of Ni	[243]
Ru	5 wt.% Ni supported on MgAl-HT	0.1/RE	Inhibits sintering; Increased activity and stability	[244]
Со	NiMgAl and NiCoMgAl-HTs	1, 4 ³⁾ /CP	Increased activity and stability	[245]
Со	NiCoMgAl-HTs	2.76-12.9/CP	nd ⁴⁾	[246]

Table 5.10 The effect of promoters on the performance of NiMgAl hydrotalcite derived catalysts in DRM.

¹⁾ Preparation methods: IMP – Impregnation; CP – Co-precipitation; RE-reconstruction in the solution of [Mⁿ⁺(EDTA)]⁽⁴⁻ⁿ⁾⁻ chelates

²⁾ nominal La/Al molar ratio

³⁾ nominal Ni/Co molar ratio

⁴⁾ nd- no data, since performance of catalyst was not compared to reference Ni-based sample

Yu et al. [239] investigated La addition into NiMgAl hydrotalcites. The effect of lanthanum was positive on both catalyst stability and activity in the temperature range of 600-700°C. La-addition increased total basicity and surface Ni content of the catalyst, resulting in the suppression of coking. The best catalytic performance was registered for the sample with nominal La/Al molar ratio of 0.11, with CH₄ and CO₂ conversions at 700°C equal to 76 and 72%, respectively. Similar positive effect of lanthanum addition in terms of catalyst stability was observed by Serrano-Lotina

et al. [240, 241]. However, the loss in catalytic activity was observed, which could be contributed to the decrease in crystallinity for La-promoted catalyst.

Lucredio et al. [242] studied La and/or Rh addition into Ni supported on MgAlhydrotalcite. The results showed that the addition of both La and Rh resulted in increased reducibility of nickel species. Thus more Ni active sites were formed on the catalyst surface. However, a negative effect of promoters addition was observed, as Rh and La promoted samples exhibited higher amounts of carbon deposits after 6h TOS DRM reaction at 750°C. On the other hand, the catalyst promoted with both Rh and La showed higher activity in terms of CO₂ conversion, but with carbon deposition still well developed.

Catalytic activity of NiMgAl and Ru-promoted catalyst was compared by Tsyganok et al. [244]. The addition of small amounts of Ru into catalyst structure by reconstruction method had a highly positive effect on the catalyst performance. Ru-promotion inhibited sintering of Ni crystallites, thus promoting higher activity and stability in comparison to the unpromoted sample. Moreover, the authors showed that a better performance of both catalysts was achieved when hydrotalcite samples were calcined/reduced in situ, and concluded that calcination prior to the reaction may result in sintering of NiO.

Li et al. [243] used Ce and Zr promoters for Ni-Mo/Mg(Al)O hydrotalcite derived catalysts. They observed increase in CH₄ conversions for samples with ceria-zirconia content below 20 wt.%. On the other hand, addition of ceria-zirconia had negative effect on CO₂ conversions. The obtained values of H₂/CO molar ratio were decreasing with the increasing content of ceria-zirconia, pointing to the promotion of RWGS reaction at 800°C. The authors confirmed the formation of a complex support of Ce_{0.8}Zr_{0.2}-Mg(Al)O which was beneficial in increasing catalyst activity. The presence of ceria-zirconia allowed the conclusion that the circulation of Ce⁴⁺/Ce³⁺ can help to eliminate the formation of coke and oxidation of carbon deposits on catalysts surface at temperatures higher than 900°C.

Long et al. [245] investigated Ni-Co bimetallic hydrotalcite-derived catalysts in DRM. The results showed that the addition of Co in an appropriate amount had a positive effect on catalyst performance. The sample with Ni/Co molar ratio equal to 4 showed the highest conversions of CO₂ and CH₄ and a stable performance in DRM at 700°C up to 100h TOS. This was explained by synergetic interactions between Ni and Co, which resulted in the formation of highly dispersed small Ni crystallites. On the contrary, Zhang et al. [246] reported the best performance of Ni-Co hydrotalcite-derived catalysts for Ni/Co molar ratios close to unity. The authors, however, noted that the amount

of metals had also effect on the catalyst performance, and catalysts with low content of Ni (1.83-3.61 wt.%) and Co (2.76-4.43 wt.%) showed better performance.

5.5.2 Advantages of hydrotalcite-derived catalysts

The comparison of catalytic performance of nickel-containing hydrotalcite-derived materials with conventional Ni-based catalyst of type Ni/support is presented in Fig 5.8, as a map of catalytic activity.

The direct comparison of catalysts presented in Fig. 5.8 is not possible, as the samples were tested in various reaction conditions. However, it is possible to conclude from Fig. 5.8, that catalysts based on hydrotalcite-like materials give higher conversions of CH₄ and CO₂ at the same reaction temperature than conventional Ni-based catalysts. The former also give similar level of conversions of CH₄ and CO₂ than the latter at lower temperatures. This clearly points to the fact that hydrotalcite-derived nickel-containing materials are promising catalysts for dry reforming of methane, as they show very high activity and stable performance. This is why, the research on these types of materials is important and may contribute to the commercialization of DRM process.

In the reports in literature concerning catalytic activity of hydrotalcite-derived materials in DRM, the authors concentrated on:

- testing materials with fixed Ni content or fixed Ni/Mg molar ratio [119, 126, 128-134], evaluation of different methods of nickel introduction,
- preparation methods [103, 127]
- or the effect of Mg/Al or M²⁺/M³⁺ [118, 120-125].

To the best of my knowledge, the effects of wide range of nickel content with fixed ratio of M^{2+}/M^{3+} (Table 5.8), zirconia promotion (Table 5.9 and 5.10) and new introduction methods of Ni, Ce and Zr species have not yet been reported. Thus, the research presented in this PhD thesis was aiming at filling that gap. The results of research on novel catalysts for chemical utilization of CO_2 via reaction of dry methane reforming is presented in the following Chapters.



Fig. 5.8 Catalytic activity map of nickel-based catalysts in dry reforming of methane reaction:
(A) CH₄ conversions and (B) CO₂ conversions as a function of temperature;
Green symbols – catalyst Ni/support: Ni/Al₂O₃-1 [81], Ni/Al₂O₃-2 [82], Ni/MgO-1 [88], Ni/MgO-2 [92], Ni/MgO-Al₂O₃
[103], Ni/CeO₂ [96], Ni/ZrO₂ [116], Ni/CeO₂-ZrO₂ [107], Ni/SiO₂ [75], Ni/SBA-15 [117], Ni/clinoptiolite [111], Ni/AC [115];
Blue symbols – hydrotalcite derived catalysts: NiMgAl-HT1 [120], NiMgAl-HT2 [122], NiMgAl-HT3 [123],
NiMgAl-HT4 [124], NiMgAl-HT5 [127], NiMgAl-HT6 [125], NiMgAl-HT7 [236], NiMgAl-HT8 [235], NiAl-HT [121];

6 Experimental

6.1 Thermodynamic analysis of DRM process

The thermodynamic equilibrium concentration analysis of DRM reaction presented in this chapter was performed with HSC Chemistry 5 software based on minimization of Gibbs free energy method (Annex 1). The effects of temperature, pressure and concentration of substrates were considered while calculating equilibrium compositions.

The possible reactants in the DRM reaction, which were taken into account during analysis, were: $Ar_{(g)}$, $CH_{4(g)}$, $C_{2}H_{2(g)}$, $C_{2}H_{6(g)}$, $CO_{(g)}$, $CO_{2(g)}$, $H_{2(g)}$, $CH_{3}OH_{(g)}$, $CH_{3}OCH_{3(g)}$, $C_{(s)}$ and $H_{2}O_{(g)}$. $Ar_{(g)}$, $CH_{4(g)}$ and $CO_{2(g)}$ were introduced into the system as the substrates, while other reactants were considered as possible products of DRM and side reactions (Table 4.2, Chapter 4.2.1).

The main goal of this part was to establish the influence of temperature, pressure, and feed gas composition on the equilibrium concentrations of possible reactants, and to compare the obtained results to literature. It is important to stress that the results of thermodynamic calculations presented in Chapter 7 were obtained assuming a closed system. Therefore, the results must be treated with caution when applied to a continuously fed system and can be seen only as an indication of the amounts of products which will be formed.

6.2 Catalysts preparation

The catalysts tested in this work were based on hydrotalcites. The general procedure applied to synthesize the materials involved co-precipitation, followed, in case of selected samples, by adsorption of transition metal species from aqueous solution of $[M^{n+}(EDTA)]^{(4-n)-}$ chelates, calcination and finally reduction/activation in the stream of hydrogen in order to obtain metallic nickel supported catalyst. The schematic procedure of the catalyst preparation is presented in Fig. 6.1.

Since the discussion of results of catalytic tests is divided into three chapters: (i) effect of nickel introduction into hydrotalcite-derived catalytic systems, (ii) effect of nickel content in brucite-like layers, and (iii) effect of promoters (Ce and/or Zr), described respectively in Chapters 8, 9 and 10, the description of the preparation procedure follows the same division. The modification procedures applied in this study are described in this chapter and the preparation details and designation of the prepared catalysts are presented in Table 6.1.



No	Name of sample	Method of Ni introduction ¹⁾	Cations in HT layers	Ni ²⁺ / Mg ²⁺	M ²⁺ / M ³⁺	Adsorption with solution of [M ²⁺ (EDTA)] ²⁻	Promoter /content
			Reference ca	talysts			
1	HT-MgAl	-	Mg ²⁺ , Al ³⁺	-	3	-	-
2	Ni/Al ₂ O ₃	IMP	-	-	-	-	-
		Influence of nic	kel introducti	on meth	nod (Cha	ipter 8)	
3	HNi-TR	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1/19	3	-	-
4	HNi-IMP	IMP	Mg ²⁺ , Al ³⁺	-	3	-	-
5	HNi-AD	AD	Mg ²⁺ , Al ³⁺	-	3	+ [Ni(EDTA)] ²⁻	-
6	HNi-CP	CP in solution of [Ni(EDTA)] ²⁻	Mg ²⁺ , Al ³⁺	-	3	-	-
		Influence of Ni lo	ading in bruci	te-like la	ayers (C	hapter 9)	
7	HNi5	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1/19	3	-	-
8	HNi15	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1/5.6	3	-	-
9	HNi25	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1/3	3	-	-
10	HNi50	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1	3	-	-
11	HNi75	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺	3	3	-	-
12	HNi100	СР	Ni ²⁺ , Al ³⁺	-	3	-	-
		Influen	ce of promote	ers (Chap	oter 10)		
13	HNi25-Ce	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺	1/3	3	+ [Ce(EDTA)] ⁻	Ce/3 wt.%
14	HNi100-Ce	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺	-	3	+ [Ce(EDTA)] ⁻	Ce/3 wt.%
15	HNi25-Zr	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺ , Zr ⁴⁺	1/3	3	-	Zr/9 ²⁾
16	HNi25-ZrCe	СР	Ni ²⁺ , Mg ²⁺ , Al ³⁺ , Zr ⁴⁺	1/3	3	+ [Ce(EDTA)] ⁻	Ce/3 wt.% Zr/9 ²⁾

 Table 6.1 The preparation details and designation of the prepared catalysts.

 $^{1)}\,\text{CP:}$ co-precipitation, IMP: impregnation, AD: adsorption,

 $^{\rm 2)}$ zirconia content expressed as Al/Zr molar ratio

6.2.1 Co-precipitation

The catalysts precursors, hydrotalcite-like materials, were synthesized by co-precipitation method at constant pH from an aqueous solution of appropriate nitrates (Ni(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O, ZrO(NO₃)₂·xH₂O – Sigma Aldrich) of total cations concentration equal to 1M. The precipitating agent was 1M solution of NaOH (POCH). These two solutions were added simultaneously to the 0.05 M solution of sodium carbonate. The flows of different solutions were adjusted in order to maintain constant pH equal to 10. The co-precipitation was carried out under constant stirring at 65°C. The obtained mineral suspension was aged at 65°C for 1h and subsequently washed with warm distilled water (ca. 50-60°C) and filtered until neutral pH of the filtrate was registered. The synthesized materials were dried in air overnight at 80°C and finally ground into fine powders.

6.2.2 Reference catalysts

In order to compare catalytic activity of different materials tested in this study and their physicochemical properties, two reference materials were synthesized. The first was magnesiumaluminium hydrotalcite-like material, which possessed the same chemical composition as naturally occurring hydrotalcite: Mg₆Al₂(OH)₁₆CO₃·4H₂O and was prepared by co-precipitation method at constant pH (sample HT-MgAl, Table 6.1).

The second reference material was nickel supported on alumina. The carrier was prepared by calcination of commercially available bohemite (SASOL) at 550°C for 4h in the stream of air. The obtained Al_2O_3 was subsequently loaded with 10 wt.% Ni by incipient wetness impregnation (sample Ni/Al₂O₃, Table 6.1).

6.2.3 Method of nickel introduction

In order to compare the influence of different methods of nickel introduction into hydrotalcite-based catalytic systems on their activity, four samples were prepared.

Nickel was introduced into brucite-like layers at the co-precipitation stage (sample HNi-TR). The amount of Ni was appropriate in order to substitute 5% of Mg²⁺ with respect to naturally occurring Mg/Al hydrotalcite mineral.

Sample HNi-IMP was prepared by incipient wetness impregnation method. The hydrotalcite powder of sample HT-MgAl was impregnated with the solution of nickel nitrate. The amount of nickel was such as to load the sample with 5wt.%. The material was subsequently dried overnight in air at 80°C and ground into fine powder.

Nickel was introduced into HNi-AD sample via adsorption method. The solution of $[Ni(EDTA)]^{2-}$ complexes was prepared by the addition of appropriate amount of nickel nitrate solution to the solution of EDTA disodium salt. The final concentration of Ni²⁺ was calculated to support HT-MgAl hydrotalcite powder with 5 wt.% of Ni. The pH of aqueous solution of [Ni(EDTA)]²⁻ complexes was adjusted to 10.5 by the addition of 1M NaOH. So prepared solution of nickel chelates was stirred with HT-MgAl hydrotalcite powder in a closed flask for 24h at room temperature, resulting in HNi-AD sample. The obtained material was filtered, washed with distilled water, dried overnight at 80°C and ground into fine powder.

The HNi-CP sample was prepared via co-precipitation method. In contrast to traditional co-precipitation, instead of Na_2CO_3 solution, precipitation was carried out in the solution of $[Ni(EDTA)]^{2-}$ complexes, prepared in the same way, as in the case of HNi-AD sample.

6.2.4 Influence of nickel loading in brucite-like layers

Materials with different content of nickel in the brucite-like layers were prepared. Nickel was introduced into hydrotalcite structure at the co-precipitation stage. The obtained nickel-containing hydrotalcites possessed fixed value of M^{2+}/M^{3+} equal to 3. The nickel content was changed by the substitution of 5, 15, 25, 50, 75 or 100% of magnesium cations by nickel cations in the brucite-like layers, with respect to naturally occurring Mg/Al hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·4H₂O). In this way, the samples designated as HNix were prepared, where x represents the percentage of Mg²⁺ cations, which were substituted by Ni²⁺.

6.2.5 The influence of promoters (Ce and/or Zr)

The effect of Ce and or Zr was examined. Ce³⁺ cations were introduced into hydrotalcitestructure via adsorption method (similarly as in the case of sample HNi-AD). The amount of Ce³⁺ corresponded to 3 wt.% of the weight of the HT-MgAl hydrotalcite powder.

Zirconium species were introduced into brucite-like layers at the co-precipitation stage. The molar ratio of Al^{3+}/Zr^{4+} was equal to 9, while molar ratio of M^{2+}/M^{3+} was equal to 3.

6.2.6 Calcination

The prepared hydrotalcite-like materials underwent calcination in order to obtain homogenous mixture of nano-oxides with periclase-like structure. The calcination was carried out in an electrically heated tubular oven. A hydrotalcite sample was heated from room temperature to 550°C in the flow of air (10cm³/min) with a heating rate of 10°C/min. The sample was kept at 550°C for 4h, and then was cooled down to room temperature.

6.2.7 Catalyst activation

Prior to each catalytic test, the catalyst sample was reduced in situ in the stream of 5% (vol/vol) H_2 in Ar. The total flow of gases was equal to $100 \text{cm}^3/\text{min}$. A catalyst sample was heated from room temperature to 900° C and then kept at this temperature for 1h. Subsequently, the catalyst sample was cooled down to the desired reaction temperature.

6.3 Characterization of the catalysts

6.3.1 X-Ray Diffraction (XRD)

The hydrotalcite precursors, the catalysts obtained upon their calcination and the samples after catalytic tests were characterized by means of XRD experiments. The diffractograms were recorded in 20 range from 8 to 90° on Empyrean diffractometer from PANalytical, equipped with a CuK α radiation source (λ =0.154059 nm).

In case of selected samples, XRD patterns were recorded as a function of temperature. A sample was placed in the resistance oven and heated from room temperature to 1000°C. The XRD diffractograms were registered at 25°C, and from 100 to 1000°C, at every 100°C.

The XRD measurements allowed to examine the structure and phase composition of the prepared samples. In case of high temperature XRD measurements, additional information concerning structure changes as a function of temperature were obtained.

The average crystal size of Ni⁰, mixed-oxides of periclase-like structure, and MgNi₃ were estimated using the Scherrer equation:

$$D_{hkl} = \frac{\kappa\lambda}{\beta_{hkl}cos\theta}$$
(eq. 6.1)

where λ is the radiation wavelength, β_{hkl} is the half-width of the reflection and Θ is the Bragg diffraction angle.

6.3.2 Infrared spectroscopy

Infrared spectroscopy measurements were carried out on Frontier spectrometer from PerkinElmer. In order to measure absorption spectra, Diffuse Reflectance Infrared Fourier Transform (DRIFT) technique was used. A hydrotalcite sample was mixed with KBr in relation 1:10 and placed in an appropriate holder. Subsequently, FTIR spectra was recorded in the range of 4000 to 450cm⁻¹.

The applied technique allowed to examine the structure of the obtained materials by the observation of characteristic absorption bands. Moreover, it allowed to confirm the introduction of transition metal species into hydrotalcites via adsorption method.

6.3.3 Low temperature N₂ sorption

The textural properties of the catalysts were determined from adsorption isotherms obtained during low temperature N_2 sorption experiments carried out on Belsorp Mini II apparatus from BEL Japan. Prior to each measurement, mixed-oxide powders were degassed under vacuum for 3 h at 110°C.

The specific surface areas of materials were calculated using BET (Brunauer-Emmett-Teller) method. The pore size distribution, mean pore diameter and volume of pores were examined by BJH (Barrett-Joyner-Halenda) analysis.

6.3.4 Elemental analysis

The catalyst elemental composition was determined by two techniques. The inductively coupled plasma mass spectrometry (ICP-MS) measurements were carried out by "SCU du CERN". The ICP-MS technique was used to examine selected samples. The second method applied in order to determine chemical composition of the tested materials was X-ray fluorescence (XRF). The measurements were carried out in an energy dispersive XEPOS spectrometer from Spectro Ametek.

The elemental analysis experiments allowed to examine chemical composition of the synthesized materials and compare the nominal values of M^{2+}/M^{3+} , Ni^{2+}/Mg^{2+} molar ratios and the content of transition metals, to the real ones.

6.3.5 Temperature Programmed Reduction (H₂-TPR)

The reducibility of the catalysts was evaluated by Temperature Programmed Reduction of H_2 (H_2 -TPR) on BELCAT-M apparatus from BEL Japan equipped with thermal conductivity detector. 50 mg of samples were degassed at 100°C for 2h. The samples were subsequently reduced in 5% (vol/vol) H_2 /Ar between 100 and 900°C at 7.5°C/min heating rate.

H₂-TPR experiments allowed to examine reducibility of the prepared materials. Thus appropriate reduction temperature of a catalyst could be established. Moreover, H₂-TPR profiles may give additional information about the type of metal species present in the catalyst and metal support interactions.

6.3.6 Temperature Programmed Desorption of CO₂ (CO₂-TPD)

The BELCAT-M apparatus from BEL Japan was used to evaluate basicity of the materials by Temperature Programmed Desorption of CO₂ (CO₂-TPD). The measurements were performed for calcined and reduced samples. The materials (60mg) were first degassed for 2h at 500°C and then cooled to 80°C. A mixture of 10% (vol/vol) CO₂/He was then introduced for 1h in order to adsorb CO₂. A flow of He was subsequently fed for 15 minutes to desorb weakly physically adsorbed CO₂. The samples were further heated up to 800°C under He flow at heating rate 10°C/min, while the evolution of CO₂ was measured with the aid of TC detector.

The total basicity of the prepared materials was calculated by means of the integration of the overall desorption profile, which was well deconvoluted into three Gaussian contributions corresponding to weak, intermediate and strong basic sites.

6.3.7 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analysis was carried out with the aid of JEOL JSM-7500F microscope coupled with INCAPentaFetx3 EDS system. The secondary electron detector provided SEM images and back-scattered electron detector provided BSE(COMPO) micrographs. The samples were coated with 20 nm Cr layer.

Recorded SEM images allowed to study morphology of the calcined and reduced materials, as well as the catalysts after DRM reaction. The EDS analysis was used to check homogeneity of the tested materials.

6.3.8 Transmission Electron Microscopy (TEM)

The catalysts before and after the DRM reaction were examined by Transmission Electron Microscopy (TEM, JOEL JEM-100CXII, acceleration voltage of 100keV). Based on the analysis of the obtained images, the distribution of nickel crystallite size was discussed. The analysis of particle size distribution involved the analysis of at least 300 Ni crystals. The measurements of Ni particle size was performed by ImageJ software.

6.3.9 Thermogravimetric measurements (TG)

Carbon formation during the DRM reaction was quantified using thermogravimetric analysis under air atmosphere. The experiments were carried out with a SDT Q600 apparatus (TA Instruments), under air flow of 100cm³/min with heating from ambient temperature to 900°C at a rate of 10°C/min.

6.4 Dry reforming of methane catalytic tests

The activity of the studied catalysts towards methane dry reforming was evaluated in a catalytic setup presented in Fig. 6.2.



Fig. 6.2 The scheme of DRM catalytic tests installation

A mixture of gases (CH₄/CO₂/Ar) was fed into U-shape reactor. The total flow was equal to 100cm³/min and was adjusted with the aid of several mass flow controllers (BROOKS). A catalyst was placed in a quartz U-shaped reactor (Fig. 6.3). The catalyst bed was supported on quartz wool. The mass of the catalyst was chosen so to work with constant value of gas hourly space velocity (GHSV) equal to 20 000h⁻¹. The reactor was placed in the resistance oven. Temperature in the oven and in the catalyst bed was controlled with the aid of thermocouples and a temperature programmer. The gaseous products of DRM reaction were passed through a water trap and subsequently analyzed by a CPi 490 Varian micro gas chromatograph equipped with COX column and a thermal conductivity detector.

The feed gas composition in most of the tests was equimolar. However, selected samples were also tested with other feed gas compositions. Additionally, some catalysts were also examined in CH_4 decomposition reaction. The catalytic set up and reaction conditions were the same for all experiments. The feed gas composition was the only parameter that changed for CH_4 decomposition and catalytic tests carried out with varied $CH_4/CO_2/Ar$ ratio. The composition of feed gas for the different types of experiments are presented in Table 6.2.

Process	Feed gas composition CH₄/CO₂/Ar	Total flow (cm ³ /min)	Temperature (°C)	GHSV (h ⁻¹)
DRM1	1/1/8	100	850→550°C, 550, 650, 750°C	20000
DRM with excess of CH ₄	1.5/1/7.5	100	550, 650, 750°C	20000
DRM with excess of CO_2	1/1.5/7.5	100	550, 650, 750°C	20000
DRM2	1.5/1.5/7	100	550, 650, 750°C	20000
CH ₄ decomposition	2/-/8	100	550, 650, 750°C	20000



Fig. 6.3 The scheme of U-shaped quartz reactor used in DRM catalytic tests

Conversions of CH_4 and CO_2 and the yield of the products, given as H_2/CO molar ratio during DRM and methane decomposition reaction, were calculated as:

$$\% CH_4 \ conversion = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \cdot 100\%$$
 (eq. 6.2)

$$\% CO_2 conversion = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \cdot 100\%$$
 (eq. 6.3)

$$\frac{H_2}{CO}molar \ ratio = \frac{F_{H_2,out}}{F_{CO,out}}$$
(eq. 6.4)

where *F_{in/out}* corresponds to the flow rate of each component in the feed or effluent.

Typically, two types of experiments were carried out, showed schematically in Fig. 6.4. In the first type (Fig. 6.4 A), a sample was first reduced in situ in the stream of H_2 in Ar. Then the catalyst bed was washed for 20 minutes with Ar and at the same time it was cooled to 850°C. The feed gas was introduced into the reactor and DRM was carried out for 30 min. Then the sample was cooled by 50°C, and the reaction was again carried out for the same duration. Such steps were repeated up to 550°C.

In the second type of experiments, DRM reaction was carried out at constant temperature. The catalyst bed, after reduction, was purged with Ar and cooled down to 550, 650 or 750°C. In a typical experiment, the catalysts were tested for 5h at 550°C. Selected catalysts were also examined at 650 and 750°C. The most active samples were additionally studied in 24h stability tests.





7 Thermodynamic analysis

7.1 The influence of temperature on equilibrium concentrations of reactants during DRM process

The results of thermodynamic equilibrium composition calculations for DRM reaction with feed gas composition $CH_4/CO_2/Ar = 1/1/8$ and their evolution with the increase of temperature are presented in Fig. 7.1. and Fig. 7.2. The conditions of DRM process were the same, as those applied in DRM catalytic tests performed in this study and described in Chapter 6.4.

CH₄ conversion was increasing with temperature and reached ca. 100% at 800°C. CO₂ conversion decreased with temperature till it reached minimum in the temperature range 500-600°C and then an increase in conversion was observed. CO₂ conversions reached ca. 100% at temperatures higher than 950°C. In the whole temperature range CH₄ conversions were higher than for CO₂, especially in the low temperature range. This clearly indicates that both methane and carbon dioxide are involved in side reactions. It is reflected also in the excess of produced H₂, especially at low temperature as illustrated by Fig. 7.1 B, where the values of H₂/CO molar ratio reached unity above 850°C. Apart from the products of DRM reaction, H₂ and CO, carbon and water were formed. The concentration of other chemical compounds that were included in the study, such as CH₃OH, C₂H₆, C₂H₄, CH₃OCH₃, HCOOH, were observed at the level of ca. $1 \cdot 10^{-3} - 1 \cdot 10^{-4}$ moles for C₂ hydrocarbons, and were even lower for the other considered chemicals, and thus the influence of reactions involving these chemicals on DRM process may be neglected and will not be discussed further.

The equilibrium water content was decreasing with the increase of temperature and only negligible amounts of water were present in the system at temperatures higher than 900°C. Water can be formed in RWGS reaction (eq. 4.2, Chapter 4.2), reduction of CO and CO₂ with hydrogen (eq. 4.5, 4.6), OCM (eq. 4.7, 4.8, Chapter 4.2) and methanation processes (eq. 4.13, 4.14, Chapter 4.2). It is most probable that in the low temperature range RWGS contributes the most to the water formation. The same conclusion was reported by Soria et. al [60], who observed that in the combined SRM-DRM process, RWGS reaction was thermodynamically most favoured at 550°C.



Fig. 7.1 The influence of temperature on the equilibrium concentration of reactants during DRM. Temperature range 300-1200°C. Atmospheric pressure.
(A) equilibrium conversions of reactants for CH₄/CO₂/Ar=1/1/8; (B) equilibrium H₂/CO molar ratio;
(C) CH₄ equilibrium conversion; (D) CO₂ equilibrium conversion;
(E) Equilibrium moles of H₂; (F) equilibrium moles of CO;



Fig. 7.2 Equilibrium moles of carbon (A) and water (B) as a function of temperature during DRM. Temperature range 300-1200°C. Atmospheric pressure.

Equilibrium carbon content was decreasing with the increase of temperature and almost no carbon formation may be observed at temperatures higher than 900°C (cp. Fig. 7.1 A and Fig. 7.2 A). Up to 550°C the amount of carbon deposits decreased slowly, and above 550°C the decrease was rapid. As is reported in literature [57-59], carbon formation at low temperatures may be mainly associated with the disproportionation of CO (eq. 4.4, Chapter 4.2). The reverse reaction is highly endothermic, and thus promoted at high temperatures, which can contribute to the oxidation of carbon deposits and results in the decrease of equilibrium carbon content. On the other hand, endothermic direct CH₄ decomposition is responsible for carbon formation at high temperatures.

The obtained values of H₂/CO ratio showed an excess of hydrogen in the system (Fig. 7.1 B, E, F), which is decreasing with the increase of temperature. This effect may be explained by the occurrence of direct methane decomposition and SRM reactions. As reported by Ozkara-Adinoglu [61] for the combined SRM-DRM process, CH₄ reacts more easily with water than CO₂, since the latter is a very stable molecule. Additionally, in the low temperature range exothermic water gas shift (WGS) can influence DRM process and contribute to H₂ production.

7.1.1 The effect of CH₄/CO₂/Ar feed gas composition on equilibrium concentrations of reactants during DRM process

The results of thermodynamic calculations with various compositions of feed gas for DRM process are presented in Fig. 7.1 B-F and Fig. 7.2. The CH₄ conversions increased with increasing content of CO₂ in the feed gas, indicating that CO₂ gas as a mild oxidant has a positive effect on CH₄ conversion. For CH₄/CO₂ > 1 ratios, CO₂ acts as a limiting reactant and cannot convert CH₄ completely. This results agrees with Le Chatelier's principle. The difference in CH₄ conversion is

mostly evident in the low temperature range, while above 900°C CH₄ conversions are at the same level, regardless of CH₄/CO₂ molar ratio.

CO₂ conversions follow the opposite trend and decrease with the increasing CO₂ content. This can be explained by the fact that as CH₄/CO₂ ratio increases, CH₄ becomes the limiting agent and cannot convert CO₂ completely. For CH₄/CO₂ ratios \geq , 1 CO₂ conversion reached ca. 100% at temperatures above 900°C. When the excess of CO₂ was present in the feed gas, CO₂ conversions reached maximum values at the level of 75 and 88%, respectively for feed gas compositions of CH₄/CO₂/Ar=1/2/7 and 1/1.5/7.5.

The trends for CH₄ and CO₂ conversions are reflected directly in the amount of obtained products. H₂ production was increasing with the increasing CH₄/CO₂ molar ratio in the gas feed, as the excess of CH₄, which did not undergo conversion in DRM reaction, was consumed by CH₄ decomposition, with the formation of H₂ (Fig. 7.1 C) and carbon (Fig. 7.2 A). Equilibrium moles of CO content were increasing with decreasing the CH₄/CO₂ ratio (Fig. 7.1 D). For CH₄/CO ratio \geq 1 almost no difference in CO equilibrium moles was observed. When the excess of CO₂ was present in the feed gas, CO production increased, due to RWGS reaction. This is directly reflected in the equilibrium concentration of water (Fig. 7.2 B). The values of H₂/CO molar ratio showed the increase of H₂ excess in the products of DRM process with increasing CH₄/CO₂ ratio, which may be explained by the occurrence of carbon-forming reactions, mainly CH₄ decomposition.

The formation of carbon deposits was decreasing with the increasing content of CO_2 in feed gas. The excess of CO_2 over stoichiometric value resulted in no carbon formation at temperatures higher than 700°C. On the other hand, with the excess of CH_4 in the feed gas carbon was observed in the whole temperature range.

The presented results of thermodynamic analysis are in agreement with those reported by Nikoo et al. [54], Li et. al [56], Shamsi et al [58], Sun et al. [59] and Ozkara-Aydinoglu [61].

7.2 The influence of pressure on reactant concentration during DRM

The possible applications of synthesis gas obtained in DRM process are FT synthesis of long chain hydrocarbons, DME or methanol synthesis. These chemical processes are carried out at high pressures (higher than 10 bar) [61], and thus the production of synthesis gas via DRM reaction at high pressures could be beneficial from the economic point of view.



(A) CH₄ equilibrium concentration; (B) CO₂ equilibrium concentration; (C) H₂/CO molar ratio; (D) carbon deposition; (E) water amount;

The influence of pressure on equilibrium reactant concentrations during DRM process is depicted in Fig. 7.3. CH₄ conversions were decreasing with the increase in system pressure (Fig. 7.3 A). Equilibrium conversions were significantly shifted to higher temperatures with pressure

increase. At very high pressures (20, 50 bars) minimum CH_4 conversion was reached between 300-550°C and for such pressures, 100% conversion was not reached even at temperatures as high as 1200°C. The effect of pressure on CO_2 conversion may be considered in two temperature regions. Between 300-550°C increasing pressure positively affected CO_2 conversion. At higher temperatures a negative effect of pressure on CO_2 conversion was observed, similarly as for CH_4 (Fig. 7.3 B). At the same time, differences between CH_4 and CO_2 conversions become smaller as the pressure increased.

Pressure also affected the distribution of the obtained products (Fig. 7.3 C). The excess of H₂ in the products of the reaction was observed when pressure increased. It may have been caused by CH₄ decomposition reaction, as at the same time the increase in carbon formation was observed with increase in pressure (Fig. 7.3 D). In the temperature range of 300-550°C high pressure can inhibit the formation of carbon, which is directly reflected in increased CO₂ conversion in the same temperature region. As reported by Shamsi et al. [58] the effect of pressure on two carbon forming reactions (CH₄ decomposition and Boudouard reaction) is different. Boudouard reaction is favoured by high pressures, while CH₄ decomposition is favourable at low pressures. At the same time CO₂ conversion may have been enhanced by RWGS, as water content in DRM process system was growing with increasing pressure (Fig. 7.3 E).

In general, high pressures have a negative effect on DRM reaction, as CH_4 and CO_2 conversions decrease and H_2/CO molar ratio, carbon deposition and a water concentration, increase with the increase in pressure. The presented results are in good agreement with those reported by Chein et al. [57], Shamsi et al. [58] and Sun et al. [59].

7.3 Thermodynamic limitations in tested reaction conditions

The equilibrium conversions of CH_4 and CO_2 and H_2/CO molar ratio relevant for the study presented in the following chapters is presented in Table 7.1.

Thermodynamic Limit	550°C	600°C	650°C	700°C	750°C	800°C	850°C
CH₄ conversion(%)	87	91	94	96	97	98	99
CO ₂ conversion (%)	45	53	67	81	90	96	98
H ₂ /CO molar ratio (-)	3.5	2.2	1.5	1.2	1.1	1.0	1.0

Table 7.1 The thermodynamic limits of CH_4 and CO_2 conversions and H_2/CO molar ratio for selected temperatures at 1bar with feed gas composition $CH_4/CO_2/Ar=1/1/8$.

8 Effect of nickel introduction

There are few reports in literature concerning different methods of nickel introduction into hydrotalcite structure as catalyst precursor for dry methane reforming [126, 127, 233]. In this study, four catalyst precursors were prepared with nickel introduced: into hydrotalcite brucite-like layers (HNi-TR), on catalyst surface by impregnation method (HNi-IMP), on catalyst surface by adsorption from solution of [Ni(EDTA)]²⁻ complexes (HNi-AD) and into hydrotalcite interlayer spaces by co-precipitation in the solution of [Ni(EDTA)]²⁻ chelates (HNi-CP). The preparation procedures for samples HNi-TR, HNi-IMP and HNi-CP were previously reported in literature [126, 127, 233].

A new method of incorporation of nickel was proposed for sample HNi-AD. Commonly, nickel is introduced into interlayer spaces of hydrotalcite by reconstruction method in the presence of $[Ni(EDTA)]^{2-}$ as reported by Tsyganok et al. [127] and Daza et al. [233]. In the presented research, steps of calcination followed by reconstruction were omitted in order to simplify the preparation procedure, which may in future have a beneficial effect from economic standpoint. As CO_3^{2-} anions exhibit high affinity to brucite-like layers, the treatment of hydrotalcite powder in the solution of $[Ni(EDTA)]^{2-}$ chelates would not result in the introduction of nickel species into interlayer spaces. However, small amounts of nickel species could be expected on the catalyst surface.

In this way, the comparison of different methods of nickel introduction with respect to the new proposed one and its influence on the catalysts activity in DRM was investigated.

8.1 Composition, structural and textural properties of the hydrotalcite and hydrotalcite-derived materials

The XRD diffractograms recorded for fresh catalyst precursors, calcined and reduced samples are presented in Fig. 8.1.

The freshly prepared materials exhibited reflections characteristic for the 3R rhombohedral layered structure of hydrotalcite (ICOD 00-014-0191). The samples HNi-TR, HNi-AD and HNi-IMP showed reflections at 2 θ equal to ca. 11, 23 and 35°, arising from the diffraction of X-rays on (003), (006) and (009) planes. In case of sample HNi-CP the shift of the first reflections to lower values of 2 θ was observed (reflections at ca. 6, 12, 18, 24°). The position of the first reflections in HTs XRD patterns is dependent on the basal spacing between layers, and thus the type of anions present between hydrotalcite layers. The shift of the first reflections observed for sample HNi-CP may be thus explained by incorporation of [Ni(EDTA)]²⁻ anions into interlayer spaces. The similar shift of the first reflection position to 2 θ of ca. 6° was observed by Tsyganok et al. [126].



Fig. 8.1 The XRD diffractograms registered for freshly prepared catalyst precursors (A), calcined (B) and reduced catalysts (C). Phase composition: \bigcirc hydrotalcite, \blacksquare MgO (periclase like structure), \blacksquare NiO, \blacktriangle NiAl₂O₄ (spinel), \square MgAl₂O₄ (spinel),), \blacklozenge metallic nickel, \triangle MgNi₃

The co-precipitation of sample HNi-CP was carried out under air. Therefore one may expect that, due to the presence of CO₂ in air and water, an additional phase of hydrotalcite with carbonate anions present in the interlayer spaces will be observed in XRD pattern. No such phase was registered, pointing to the successful incorporation of [Ni(EDTA)]²⁻ complexes into interlayer spaces of hydrotalcite.

All samples exhibited rhombohedral symmetry, thus parameter c of unit cell may be calculated from the position of the first reflection (eq. 8.1) or by averaging the positions of the first three reflections (eq. 8.2) [193]:

$$c = 3d(003)$$
 (eq. 8.1)

$$c = d(003) + 2d(006) + 3d(009)$$
 (eq. 8.2)

where: d(hkl) - basal spacing calculated from the position of appropriate reflections. In 3R symmetry, the unit cell of hydrotalcite is built of three layers, thus parameter*c*' describing basal spacing between two neighbouring layers was calculated. The values for all synthesized hydrotalcites are presented in Table 8.1. For, the reference and HNi-TR, HNi-IMP, HNi-AD samples*c*' was between 7.76-7.84 Å, which is close to the value 7.65 Å reported for carbonate-containing hydrotalcites [185]. A small increase in the values of parameter*c*' may suggest that the synthesized materials might, partially, also contain nitrate anions (*c*' characteristic for NO₃⁻ = 8.79 Å). As expected, the preparation procedure of sample HNi-AD did not result in the exchange of carbonate anions with [Ni(EDTA)]²⁻, and no shift in the reflections and no increase in*c*' parameter were observed. Additionally, samples HNi-AD and HNi-IMP, where nickel was introduced onto the surface of hydrotalcite, did not show any reflections arising from nickel compounds, pointing to either introduction of very small amounts of Ni or high dispersion of Ni species, making them undetectable by XRD analysis.

6l.	Unit cell	parameters	• ·····
Sample	a (Å)	<i>c′=c</i> /3 (Å)	Anions in interlayer spaces
HT-MgAl	3.06	7.84	CO ₃ ²⁻ and NO ₃ ⁻
HNi-TR	3.06	7.84	CO ₃ ²⁻ and NO ₃ ⁻
HNi-IMP	3.06	7.76	CO ₃ ²⁻ and NO ₃ ⁻
HNi-AD	3.06	7.76	CO ₃ ²⁻ and NO ₃ ⁻
HNi-CP	3.06	14.12	[Ni(EDTA)] ²⁻

Table 8.1 The unit cell parameters and anions present in the interlayer spaces of synthesized hydrotalcites

The position of the first reflection from the doublet registered close to 60° 2 θ was used to calculate parameter *a* of the unit cell (eq. 8.3, Table 8.1), which describes average cation-cation

distance in brucite-like layers. All samples exhibited values of *a* equal to 3.06 Å, indicating that no changes in the hydrotalcite structure had occurred, regardless of the preparation method.

All materials after calcination in air for 4h at 550°C exhibited reflections at 20 equal to ca. 43 and 62.5°, characteristic for periclase-like structure of mixed oxides formed via thermal decomposition of HTs (ICOD 00-045-0946). No additional phases were registered for samples HT-MgAl, HNi-TR and HNi-CP. On the other hand, samples HNi-IMP and HNi-AD exhibited additionally small intensity reflections arising from hydrotalcite, suggesting an incomplete decomposition of lamellar hydrotalcite structure. As for these two samples nickel was introduced onto the surface of hydrotalcite, it may be concluded that it resulted in the stabilization of lamellar structure. Thus higher temperature of calcination or longer calcination time should be applied in order to obtain pure phase of mixed nano-oxides.

Nickel oxide possesses the same structure as MgO, thus the main reflections in XRD patterns of these phases have the same positions. The XRD diffractograms of these oxides differ only in the position of the reflection arising from the X-ray diffraction on (111) planes, which appears at ca. 36° for MgO (ICOD 00-045-0946) and 37.5° 20 for NiO (ICOD 01-073-1519). The additional reflection at 37.5° 20 was observed for samples HNi-IMP and HNi-CP, pointing to the formation of separate NiO phase on catalysts surface.

Comulo	Ni	Mg	AI	Ni/Mg	M ²⁺ /M ³⁺
Sample	(wt.%) ¹⁾	(wt.%) ¹⁾	(wt.%) ¹⁾	molar ratio ²⁾	molar ratio ²⁾
HT-MgAl	-	37.4	14.15	-	2.98 (3.0)
HNi-TR	2.8	37.9	15.2	0.03 (0.05)	2.94 (3.0)
HNi-IMP	7.3	31.1	11.7	_3)	2.98 (3.0)
HNi-AD	0.8	21.7	8.4	_3)	2.92 (3.0)
HNi-CP	7.7	18.4	7.1	_3)	2.90 (3.0)

Table 8.2 The chemical composition of the synthesized materials

¹⁾ determined by XRF experiments

²⁾ in parenthesis nominal values are given

³⁾ nickel is present in the catalyst outside brucite-like layers of hydrotalcite

The chemical composition of the calcined samples determined by XRF analysis is presented in Table 8.2. The nickel content in the synthesized samples varied depending on the method of the material preparation. The lowest content of Ni, less than 1%, was found for sample HNi-AD, suggesting that adsorption technique may be used to introduce very small amounts of nickel into hydrotalcite-based catalytic systems. Samples HNi-IMP and HNi-CP exhibited similar content of Ni equal to ca. 7-8%. The incorporation of Ni species into brucite-like layers resulted in the sample with ca. 3 wt.% of Ni.

The calculated value of M²⁺/M³⁺ molar ratio for sample HT-MgAl (the parental material for samples HNi-IMP and HNi-AD) was very close to the nominal one. A small decrease in the value of this parameter was observed for smple HNi-AD, suggesting that during adsorption procedure with the solution of [Ni(EDTA)]²⁻ complexes, partial leaching of divalent cations may have occurred. Nevertheless, for all samples the real values of M²⁺/M³⁺ molar ratios, as well as the value of Ni²⁺/Mg²⁺ in case of sample HNi-TR, were very close to the nominal ones assumed at the step of materials preparation, proving that the composition of hydrotalcites and hydrotalcite-derived materials may be strictly controlled.

The FTIR spectra recorded for freshly prepared hydrotalcites are presented in Fig. 8.3. All samples exhibited a number of common absorption bands observed at 3550, 3000, 1650, 1370 and 870cm⁻¹. The broad band at 3550 cm⁻¹ arises from the stretching vibration of structural OH⁻ groups in the metal hydroxide layer. The position of the maximum of this absorption band may be shifted to higher wavenumber values, depending on the value of *x* i.e. the molar ratio of tri-valent cations. E.g. for high values of *x* (*x* = ca. 0.4), this absorption band was observed at 3700cm⁻¹ [185]. A small shoulder at ca. 3000cm⁻¹ may be attributed to a second type of OH⁻ stretching vibrations of interlayer hydrogen bonding with carbonate groups. The weak band at 1650cm⁻¹ was ascribed to interlayer water molecules. The strong band at 1370cm⁻¹ and weak band at 870cm⁻¹, were attributed to the stretching vibration and out-of-plane bending vibration of CO₃²⁻, respectively [189]. The bands in the range of 450-700cm⁻¹ are typical of the frameworks of HTs, and indicate M-O-M stretching, which further confirms that the catalysts precursors are ordered hydrotalcites [128].

The samples HNi-AD and HNi-CP exhibited additionally absorption bands associated with EDTA molecules. The band at 2930 and 2850cm⁻¹ are ascribed to asymmetric and symmetric C-H stretching of methylene groups. The absorption of infrared radiation by asymmetric stretching of coordinated and uncoordinated COO⁻ groups may be attributed to the bands at 2850 and 1600cm⁻¹, respectively, while band at 1110cm⁻¹ to the vibration of C-N single bonds [126, 128]. The spectra of other samples did not exhibit these adsorption bands, pointing to the fact, that [Ni(EDTA)]²⁻ species were present only in the HNi-AD and HNi-CP samples. These results stay in line with the XRD measurements which confirmed the presence of nickel-EDTA chelates between brucite-like layers for sample HNi-CP. In case of sample HNi-AD, the [Ni(EDTA)]²⁻ species were most probably deposited on the external surfaces of hydrotalcite crystals.

In the spectra of samples HNi-TR, HNi-IMP and HNi-AD a small adsorption band at ca. 1376cm⁻¹ was observed. This band, which is indicating the presence of NO₃⁻ anions [247], is in good agreement with the values of c' parameters calculated from XRD measurements.



Fig. 8.2 FTIR spectra of uncalcined hydrotalcite samples

The textural features of the hydrotalcite-derived catalysts are summarized in Table 8.3. Fig. 8.3 shows the pore size distribution and N₂ adsorption/desorption isotherms of the prepared materials. The obtained isotherms, with the exception of sample HNi-CP, may be classified as type IV according to IUPAC, which is typical for mesoporous materials. All four samples exhibited also H3 type hysteresis loop, ascribed to solids consisting of aggregates or agglomerates of particles forming slit-shaped pores with nonuniform size and shape [248, 249].

The samples exhibited specific surface areas between 100-230 m²/g, in agreement with the data reported in literature for similar hydrotalcite-derived oxides [127, 185]. The values of S_{BET} for samples HNi-IMP and HNi-AD are close to the one measured for their parental material – sample HTMg-Al, suggesting that the modification via adsorption method and impregnation of nickel species did not significantly influence specific surface area of the materials. On the other hand, a small decrease in both mean pore diameter and total pore volume was observed. The substitution of a small part of Mg^{2+} by Ni^{2+} in hydrotalcite brucite-like layers for sample HNi-TR, resulted in the increase of S_{BET} and the decrease of pore volume and size.



Fig. 8.3 N_2 adsorption/desorption isotherms and pore diameter distribution of the studied catalysts: HT-MgAl, HNi-TR, HNi-IMP, HNi-AD and HNi-CP
Sample	S _{BET} (m²/g)	V _{tot} (cm ³ /g)	Mean pore diameter (nm)
HT-MgAl	95	0.87	35
HNi-TR	166	0.74	18
HNi-IMP	102	0.83	34
HNi-AD	97	0.60	25
HNi-CP	230	0.36	6

Table 8.3 Textural properties of hydrotalcite-derived mixed oxides

Sample HNi-CP exhibited the highest value of specific surface area, which was caused by the substitution of carbonate anions by $[Ni(EDTA)]^{2-}$ complexes, resulting in the increase of basal spacing between hydrotalcite layers. The shape of N₂ adsorption isotherm and the distribution of pores measured for sample HNi-CP also differed from other materials. Narrow pores and the shape of adsorption/desorption isotherm suggest the formation of microporous material. Moreover, the observed hysteresis loop was of type H4, pointing to uniform distribution of slit shaped pores [248, 249]. This clearly indicates that the type of anions present in the interlayer spaces of hydrotalcite has a strong influence on textural properties of the studied materials.



Fig. 8.4 The TEM images recorded for samples HNi-TR (A and B), HNi-IMP (C) and HNi-AD (D)

TEM images recorded for selected samples are presented in Fig. 8.4. Samples HNi-TR, HNi-AD and HNi-IMP showed the same type of morphology, typical for hydrotalcite-derived mixed oxides. The plate/flake-like shaped particles oriented in different directions were observed. The high resolution images (Fig. 8.4 B) confirmed the lamellar structure of hydrotalcite with average planar distance around 5-6 Å. The TEM and EDX analysis showed that the samples were well crystallized and homogenous. No separate phase of nickel oxide was observed for HNi-TR sample, indicating that nickel species after calcination were incorporated into the structure of Mg(Ni,Al)O periclase-like oxides.

8.1.1 The influence of calcination temperature on hydrotalcite structure

Selected samples (HT-MgAl and HNi-AD) were studied in situ in XRD experiments performed with the increase in temperature in the range of 25-1000°C, in order to determine the influence of calcination temperature on their phase composition. The registered diffractograms are presented in Fig. 8.5.

Both samples exhibited reflections typical for layered hydrotalcite structure at temperatures 25, 100, 200 and 300°C. It is worth mentioning that the position of the first reflection was shifted to higher values of 20 with the increase in temperature, indicating structural changes of the material caused by decomposition of carbonate anions. No presence of reflections attributed to hydrotalcite structure was observed at temperatures higher than 300°C for sample HT-MgAl. On the other hand, sample HNi-AD showed low intensity reflections originating from HTs structure also at 400 and 500°C, suggesting that Ni species on the catalyst surface stabilized hydrotalcite structure, in agreement with XRD results obtained for HNi-AD sample after calcination at 550°C (Fig. 8.1). For both materials, over 400°C, reflections characteristic for periclase-like structure of mixed oxides Mg(Al)O were observed at 20 equal to ca. 43 and 63°. These reflections are observed up to 1000°C and their intensity was increasing with the increase in temperature, pointing to the growing Mg(Al)O phase crystallinity. As reported in literature [185, 186], calcination of HTs at temperatures higher than 500-600°C results in the disappearance of the ability of these materials to reconstruct their layered structure. This is explained by the increase in periclase-like phase crystallinity and the formation of spinel phases.

Additional reflections originating from the spinel phase of MgAl₂O₄ were observed at XRD diffractograms for both samples at 900 and 1000°C. They were registered at 20 of ca. 37, 44, 59 and 65°, and are attributed to the diffraction of X-rays on (311), (400), (511) and (440) planes. Other reflections originating from MgAl₂O₄ were also observed at higher values of 20 (ICOD 01-077-1193), however, as the quality of diffractograms registered in high temperature program was lower than the ones registered at room temperature, they are not well visible on Fig. 8.5. The obtained results

indicate the co-existence of two phases at 900 and 1000°C i.e. spinel and periclase-like mixed oxides. The crystallinity of both increases with the increase in temperature.



Fig. 8.5 The XRD diffractograms registered for samples HT-MgAI (A) and HNi-AD (B) in the temperature range of 25-1000°C; — hydrotalcite structure, — periclase-like structure of Mg(AI)O oxides; — coexistence of spinel phase and Mg(AI)O periclase-like oxides

As mentioned in Chapter 5, the formation of spinel phases is highly dependent on the composition of HTs. In case of the studied samples, the reflections arising from spinel phase were observed only after heating the samples up to 900°C. However, the formation of spinel phase at lower temperatures cannot be totally excluded. There is a possibility that they were present in small amounts and thus were beyond XRD detection limit.

The XRD diffractograms registered above 100°C for both tested samples exhibited also reflections indicating the presence of alumina. HTs, while heated, may lose up to 40% wt.% of their initial weight, which is also connected with the decrease of the powder volume. Since HTs powders studied in the high-temperature XRD experiments were placed in a holder made from Al₂O₃, the reflections arising from alumina phase were expected. As it was reported in literature [190, 231], upon heating of pure hydrotalcite material, no separate phase of alumina should be formed. Thus reflections arising from the holder material were not taken into account, while analysing thermal behaviour of the studied powders.

8.2 The structural properties of the reduced catalysts

The hydrotalcite-derived mixed-oxides were reduced at 900°C in order to be tested for DRM process and their phase composition was subsequently analysed by XRD measurements (Fig. 8.1 C). All samples exhibited reflections arising from periclase-like structure of Mg(Al)O mixed oxides. Samples HNi-TR, HNi-IMP and HNi-CP showed also reflections typical for metallic nickel at 20 of 44.5, 51.5 and 76° (ICOD 01-087-0712). The reflection at 20 equal to 51.5° was also observed for sample HNi-AD, suggesting that upon reduction nickel species sintered to form crystals detectable by XRD. The most intense reflection arising from metallic nickel at 44.5° was overlapping with (111) reflection of Mg(Al)O phase for sample HNi-AD. Samples HNi-TR and HNi-IMP showed also the presence of MgNi₃ phase (reflections at 20 42, 48, 71 and 87°, ICOD 04-016-6336), while for sample HNi-CP an additional NiAl₂O₄ spinel phase was detected (reflections at 20 19, 31, 37, 45, 59, 65°; ICOD 01-073-0239). The phase composition of the catalysts differed, depending on the method of material preparation, which may influence catalytic activity in DRM reaction.

Basing on the reflection arising from Ni(200) planes the size of nickel crystallites was calculated for samples HNi-TR, HNi-IMP and HNi-CP, which were equal to 5, 12 and 12nm, respectively.

Fig. 8.6 shows the TEM micrographs and distribution of nickel particle size obtained for two selected samples (HNi-TR and HNi-IMP) after treatment with H₂ at 900°C. Upon reduction nickel species were extracted from periclase-like phase and formed small crystallites of nickel on the surface of Mg(Al)O oxides in case of sample HNi-TR. The introduction of nickel species via impregnation method resulted in the formation of larger nickel crystallites in comparison to HNi-TR sample, with an average size of 12-13nm. These results are in agreement with XRD analysis.

SEM images acquired for reduced samples HNi-IMP, HNi-AD and HNi-CP are presented in Fig. 8.7. On the recorded images, plate/flake-like shaped particles may be distinguished. Small and

bright particles appear on the surface of such flakes. It seems that the amount and distribution of these particles is dependent on the material preparation method.



Fig. 8.6 TEM images and the corresponding histograms for the catalysts: (A) HNi-TR and (B) HNi-IMP



Fig. 8.7 SEM micrographs for reduced samples HT-IMP (A), HNi-AD (B) and HNi-CP (C and D)

8.3 Reducibility of Ni species and acid-base properties

The H₂-TPR profiles obtained for the calcined hydrotalcite-derived catalysts are presented in Fig. 8.8. The reference HT-MgAl sample did not exhibit any reduction peaks, due to the lack of nickel species. For all nickel-containing samples, the reduction peak temperatures ranged from 388 to 890°C, suggesting various types of interaction between NiO species and the mesoporous Mg(Al)O support. According to literature, pure NiO phase is reduced at the temperature range of 220-420°C. Li et al. [250] showed one reduction peak of bulk NiO centered at 220°C. Mile et al. [251] reported that bulk NiO gave two reduction peaks: (i) at 250°C arising from reduction of Ni³⁺ species and (ii) at 400°C ascribed to the reduction of Ni²⁺ species. The data reported by Kadkhodayan et al. [252] and Daza et al. [233] showed, respectively, a doublet of peaks and one peak at the temperature range of 300-400°C for bulk NiO. Thus, it can be stated that the reduction peaks centred at 388, 420 and 480°C and recorded for samples HNi-IMP, HNi-TR and HNi-CD were associated with the reduction of bulk NiO particles weakly interacting with catalysts surface [233, 251, 252].





The most intense reduction peaks for all catalysts were observed at the temperature range of 600-900°C, indicating strong interactions between nickel species and the support. These peaks may be thus attributed to the reduction of Ni²⁺ in NiO-MgO solid solution or NiAl₂O₄ spinel phase [128]. The highest temperatures of reduction were observed for the samples synthesized by adsorption and impregnation methods. The XRD profiles for reduced samples HNi-IMP and HNi-AD did not show the formation of spinel phase, thus, most probably, NiO particles distributed on

catalyst surface formed a solid solution with MgO. Such high temperature of reduction indicated also high dispersion of nickel species on catalysts surfaces.

The reduction peak cantered at 785°C observed for sample HNi-CP may be ascribed to the reduction of nickel species from NiAl₂O₄ spinel phase, which was confirmed by XRD results (Fig. 8.1. C). Nickel was introduced into brucite-like layers of hydrotalcite in case of sample HNi-TR. As claimed by Daza et al. [236], the reduction of Ni²⁺ species becomes only possible in Ni-O-Ni species and not in Ni-O-Mg species, which indicates that Ni needs to be first extracted from the solid solution and then reduced to Ni⁰. The content of Ni in sample HNi-TR was at a level of ca. 3 wt.%, which means that Ni species were well distributed in the framework of Mg(Ni,Al)O, and most probably were surrounded by magnesium species, forming in this way mostly Mg-O-Ni species, and thus high temperature of reduction was required.

The study of H_2 -TPR profiles of the prepared catalysts showed that reducibility varied depending on the method of nickel introduction into hydrotalcite-based catalytic systems and increased in the following sequence: HNI-IMP > HNI-AD > HNI-TR > HNI-CP.

The basicity of the prepared catalysts was investigated by CO₂-TPD experiments, and the results are presented in Fig. 8.9 and Table 8.3. As reported in literature, the basicity of hydrotalcitederived materials depends on the composition of the catalyst precursor (layer composition and type of anions present between layers) [199, 201]. Di Cosimo et al. [197] reported, based on the IR and CO₂-TPD data, that hydrotalcite-derived mixed oxides exhibit typically three overlapping desorption peaks: (i) the first one observed between 100-150°C is attributed to the desorption of CO₂ from weak Brønsted OH⁻ groups, (ii) the second observed at ca. 190°C is assigned to the formation of bidentate carbonates formed on metal-oxygen pairs (Lewis acid-base pairs) and (iii) the third ascribed to strong basic sites observed at ca. 280°C, originating from the desorption of CO₂ bonded with low-coordination oxygen anions (cp. Chapter 5.2.3, Fig. 5.4). The calcined and reduced catalysts exhibited one asymmetric desorption peak formed by superposition of these three peaks (Fig. 8.9).

The total basicity of the calcined materials was in the range of 180-250µmol/g and decreased in the sequence: HNi-TR > HT-MgAl (reference sample) > HNi-CP > HNi-IMP > HNi-AD. The method of nickel introduction influenced strongly the basicity of materials. Sample HNi-TR exhibited higher amount of basic sites than sample HT-MgAl, indicating that the substitution of Mg²⁺ by Ni²⁺ increases basicity of HTs-derived mixed oxides. On the other hand, the samples, into which nickel was introduced onto hydrotalcite surface (HNi-IMP and HNi-AD), showed the lowest amount of basic sites, indicating some blockage of basic sites, most probably by the blockage of

pores, in good agreement with N₂ sorption results. The distribution of weak, medium and strong basic sites, calculated by the Gaussian deconvolution of CO₂-TPD profiles (Table 8.4), showed that the samples did not differ in this distribution and exhibited ca. 20, 30 and 50% of weak, intermediate and strong basic sites, respectively.



Fig. 8.9 The CO₂-TPD profiles recorded for calcined catalysts (A) and catalysts after activation in the stream of hydrogen (B)

Calcined samples				Reduced samples				
Sample	W ¹⁾	M ²⁾	S ³⁾	Total	W ¹⁾	M ²⁾	S ³⁾	Total
	(%)	(%)	(%)	(µmol/g)	(%)	(%)	(%)	(µmol/g)
HT-MgAl	16	30	54	231	30	58	12	93
HNi-TR	18	32	50	250	34	56	10	60
HNi-IMP	18	31	51	205	19	51	30	74
HNi-AD	17	29	54	183	37	50	13	40
HNi-CP	19	32	50	212	19	54	27	70

¹⁾percentage of weak basic sites; desorption peak T<200°C

²⁾percentage of basic sites of medium strength; desorption peak 200°C<T<300°C

³⁾percentage of strong basic sites; desorption peak T>300°C

For all calcined samples one additional desorption peak was registered at the temperature range of 600-800°C (results not shown), which might be attributed to the completion of

dehydroxylation processes and decomposition of carbonate anions, which were not completely removed during calcination [253, 254].

The shape of CO₂-TPD profiles and the distribution of basic sites drastically changed after activation of catalysts in the stream of 5%H₂ in Ar (Fig. 8.9B, Table 8.3). In general, the shift of the peaks ascribed to intermediate and strong basic sites to higher temperatures was observed, in good agreement with the results presented by Abello et al. [253]. Moreover, total basicity of the materials decreased by one order of magnitude and formed a the sequence: HT-MgAl > HNi-IMP > HNi-CP > HNi-TR > HNi-AD. Samples HT-MgAl, HNi-TR and HNi-AD showed similar distribution of basic sites, while samples HNi-CP and HNi-IMP exhibited the highest distribution of basic sites associated with O^{2-} anions with respect to other catalysts.

8.4 Activity and selectivity in DRM

8.4.1 Catalytic tests at temperature range 550-850°C

Fig. 8.10 presents the results of the DRM catalytic experiments measured under steadystate conditions and carried out at the temperature range of 550-850°C and in the presence of different catalysts. CH_4 and CO_2 conversions increased with temperature, due to high endothermicity of DRM reaction. Samples HNI-IMP, HNI-AD and HNI-CP showed very similar performance, especially at temperatures above 700°C. The activity in the view of both CH_4 and CO_2 conversions followed the sequence: HNI-IMP > HNI-AD > HNI-CP >> HNI-TR. The obtained values of H_2/CO molar ratio (Fig. 8.10 C) were lower than unity and were increasing with the increase of temperature. The differences between samples were visible at temperatures lower than 700°C. These results indicate that the DRM process was influenced by reverse water gas shift (RGWS) reaction. The obtained values of CO_2 conversions were higher than CH_4 conversions for all tested catalysts, which also confirms the influence of RWGS on the overall process.

The lowest activity was exhibited by the sample into which nickel was introduced into brucite-like layers. Considerable conversions of CH₄ and CO₂ for this sample were observed above 800°C. Similar materials were reported to be very efficient catalysts in DRM reaction [120, 125], however, the reported materials were loaded with higher amounts of nickel. Thus, most probably the lowest activity of sample HNi-TR was caused by low nickel content. The nickel species were well dispersed in the Mg(Ni,Al)O solid solution, making them hard to reduce and thus inactive in DRM.

Surprisingly, the HNi-AD sample, loaded with less than 1 wt.% of Ni, showed comparable performance to catalysts with 7 times higher nickel content (samples HNi-IMP and HNi-CP). This

high activity may be attributed to the fact that the introduction of nickel species by adsorption of [Ni(EDTA)]²⁻ complexes resulted in the formation of separated and very small (undetectable by XRD) aggregates on catalyst surface. This stays in line with H₂-TPR results, as this sample exhibited the highest reduction temperature, indicating the presence of small well dispersed nickel species. Therefore, it can be stated that sample HNi-AD showed the highest activity per gram of active material in DRM reaction.

The highest activity per gram of catalyst was shown by impregnated HNi-IMP sample, which reached thermodynamic limit of CO₂ conversion at 850°C. The high activity of the catalyst may be attributed to the highest total basicity with respect to other materials. The HNi-IMP sample exhibited also the highest distribution of strong basic sites (low coordination O²⁻anions), which facilitate activation of CO₂, especially at low reaction temperatures. Sample HNi-IMP showed also (together with sample HNi-CP) the largest size of Ni crystallites around 12 nm, confirmed by XRD and TEM analysis. Thus it is possible that high activity in terms of CH₄ and CO₂ conversions was enhanced by the occurrence of side reactions, i.e. carbon forming reactions, such as CH₄ decomposition and disproportionation of CO, which proceed more easily on big crystallites of Ni [73].

Sample HNi-CP showed slightly lower conversions of CH₄ and CO₂ than sample HNi-IMP. Both samples exhibited similar mean size of nickel crystallites around 13 nm. However, contrary to sample HNi-IMP, in the XRD pattern of reduced HNI-CP sample additional phase of NiAl₂O₄ was observed. As it was reported in literature, the formation of spinel phase may block reduction of nickel species, due to the strong metal-support interactions, and thus limit the formation of active centres for DRM.

As catalysts may have underwent some structural changes upon reaction in the temperature range of 550-850°C, the XRD experiments for catalyst after reaction were performed (Fig. 8.11). In comparison to XRD diffractograms recorded for the samples after activation in H₂ (Fig. 8.1 C), some phase transformation may be observed for all samples. In general, all catalysts exhibited the increase in intensity of reflections attributed to the periclase-like structure of mixed oxides, pointing to the increase of crystallinity of this phase. This was confirmed by the estimation of Mg(Al)O crystal size and increase of crystal size from ca. 2-3nm to 4-5nm observed for all catalysts.



Fig. 8.10 The results of catalytic tests carried out in temperature range 550-850°C: (A) CH₄ conversion, (B) CO₂ conversion, (C) H₂/CO molar ratio; GHSV=2000h⁻¹, total flow 100cm³/min, CH₄/CO₂/Ar=1/1/8

The Ni crystallite sizes calculated for the reduced and spent catalysts are presented in Table 8.4. The sintering of nickel particles was observed for the most active catalyst (HNi-IMP), which may cause deactivation of catalyst in long-term catalytic tests. On the other hand, for the HNi-CP catalyst the decrease in Ni crystallite size was observed. This phenomenon is rather difficult to explain, and additional research should be carried out in order to clearly understand it. One possible explanation is, that during reaction at high temperatures, nickel species react with support resulting in the formation of a new phase e.g. NiAl₂O₄, which separates Ni crystallites. As spinel phase is inactive in DRM reaction, this could explain why the activity of the sample in terms of CO₂ conversion was slightly higher than the one observed for HNi-AD catalyst at 850 and 800°C.



Fig. 8.11 The XRD diffractograms recorded for catalysts after DRM tests at the temperature range 550-850°C: \blacksquare periclase-like phase of Mg(Al)O mixed oxides, \bullet metallic nickel, \Box MgAl₂O₄ spinel phase, \triangle MgNi₃ \blacksquare graphitic carbon

Sample		Ni crystallite size ¹⁾ (nm)				
Sample	Reduced	After tests at 550-850°C	After tests at 550°C			
HNi-TR	5	5	6			
HNI-IMP	12	16	14			
HNi-AD	No phase of metallic Ni was detected by XRD					
HNi-CP	12	7	13			

Table 8.5 The Ni crystallite size estimated for the reduced catalysts and those after catalytic tests carried out at the temperature range of 550-850° and at 550°C

¹⁾estimated by Scherrer equation, based on the position of Ni(200) reflection

8.4.2 Low temperature DRM (isothermal tests at 550°C)

The catalytic activity of the prepared DRM catalysts was also examined during isothermal 5h-catalytic tests at 550°C (Fig. 8.12). At temperature as low as 550°C, the different Ni-containing

hydrotalcite-derived materials showed good catalytic performance. The activity in terms of CH₄ and CO₂ conversion decreased in order: HNi-IMP > HNi-CP > HNi-TR > HNi-AD and followed nickel content and total basicity of tested catalysts. With the exception of the HNi-AD sample, the catalysts did not show any deactivation during 5h catalytic tests, pointing to, either the formation of non-poisonous carbon deposits, or no carbon formation. Similarly as in case of catalytic tests carried out at the temperature range 550-850°C, the obtained conversions of CO₂ were higher than those of CH₄, indicating the occurrence of RWGS, which is directly reflected in the obtained values of H₂/CO molar ratio below unity.

Again the most active catalyst turned out to be the impregnated one. Similar performance was shown by sample HNi-CP. The characterization of the prepared materials revealed that these two catalysts exhibited very similar properties, such as nickel content, Ni particle size and total basicity. In terms of catalytic activity, the high basicity of materials seems to be the main driving factor for their good performance. Both catalysts showed similar basicity after activation in H₂ equal to ca. 70µmol/g and more importantly, in comparison to other catalysts they were characterized by the highest distribution of strong basic sites of around 30%. The highest amount of strong basic sites seems to enhance catalytic activity. The activity of HNi-CP catalyst lower than for HNi-IMP may be explained by the formation of inactive NiAl₂O₄ spinel phase in case of the former.

The constant decrease in CH_4 and CO_2 conversions was observed in case of sample HNi-AD. As material exhibited very strong interactions between nickel active phase and support (confirmed by H₂-TPR) sintering of nickel species was probably not the main cause of catalyst deactivation. The decreasing values of H₂/CO molar ratio suggest that RWGS reaction affected the overall DRM process to more extent with the growing TOS.

It is worth mentioning that the results presented in Fig. 8.12 differed from the ones registered under temperature programmed conditions i.e. starting at 850°C and followed by cooling down to consecutive temperatures until 550°C (cp. Fig. 8.10). The recorded values of CH_4 and CO_2 conversions were much higher during isothermal experiments than in temperature-programmed catalytic tests. The activity sequence was also different, which indicates some structural and phase changes in the materials, induced by their initial heating at 850°C, e.g. the formation of spinel phases or sintering of Ni crystallites. In order to investigate this issue, XRD diffractograms of catalysts after isothermal tests (Fig. 8.13) were recorded and compared to the ones obtained after temperature programmed conditions. Based on the obtained results Ni particle sizes were also estimated (Table 8.5).



Fig. 8.12 The results of isothermal DRM catalytic tests carried out at 550°C: (A) CH₄ conversion, (B) CO₂ conversion, (C) H₂/CO molar ratio; GHSV=20000h⁻¹, total flow 100cm³/min, CH₄/CO₂/Ar=1/1/8

Similarly as in the case of temperature-programmed conditions, catalysts after the tests at 550°C showed increase in intensity of reflections originating from the phase of mixed-oxides. Additionally, the increase in intensity of the reflections arising from metallic nickel phase was observed for samples HNi-IMP and HNi-CP, pointing to sintering of nickel particles upon reaction, which was confirmed by the values calculated by Scherrer equation. In case of sample HNi-CP, contrary to the results obtained after the test at the temperature range of 550-850°C, no reflections originating from spinel phase were observed, which explains higher activity of this catalyst under isothermal conditions.

The additional reflection at 20 equal to ca. 26° was registered for sample HNi-IMP, indicating the presence of graphitic carbon on the catalyst surface. The formation of carbon deposits was most probably the result of sintering of Ni crystallites, as C-forming reactions proceed more easily on big Ni particles. This reflection was not observed in XRD patterns of any other sample, suggesting that no graphitic carbon was formed on their surface upon DRM reaction. However, the formation of amorphous carbon deposits cannot be excluded.



Fig. 8.13 The XRD diffractograms recorded for catalysts after DRM tests at 550°C: ■ periclase-like phase of Mg(AI)O mixed oxides, ● metallic nickel, ○ meixnerite (hydrotalcite) △ MgNi₃ ▼ graphitic carbon

Interestingly, in case of sample HNi-TR, the reflections at 20 equal to 11, 23 and 35° were registered, characteristic for layered hydrotalcite structure. It was mentioned before that HTs possess the ability of reconstructing their layered structure in the presence of aqueous environment. Thus, most probably water formed in RWGS reaction allowed sample HNi-TR to form meixnerite phase (a mineral in the group of hydrotalcites with OH⁻ anions present in the interlayer

spaces; ICOD 00-050-01684). This is in agreement with low values of H₂/CO obtained over HNi-TR catalyst.

8.5 Conclusions

The hydrotalcite-derived materials were synthesized and tested in DRM reaction. Nickel species were introduced into the HT-based catalytic systems via four methods: (i) co-precipitation in the solution of Na₂CO₃ leading to Ni species introduced into brucite-like layers, (ii) impregnation method leading to Ni species introduced on HT surface, (iii) adsorption from the solution of [Ni(EDTA)]²⁻ complexes leading to Ni specie introduced on HT surface and (iv) co-precipitation in the solution of [Ni(EDTA)]²⁻ species leading to Ni species introduced on HT surface and (iv) co-precipitation in the solution of [Ni(EDTA)]²⁻ species leading to Ni species introduced into interlayer spaces of hydrotalcite. The physico-chemical characterization of the prepared materials showed that all catalysts were successfully loaded with Ni and that their properties were dependent on the method of nickel introduction.

The temperature programmed and isothermal catalytic tests revealed that the highest activity was shown by the impregnated sample, which was most probably attributed to high dispersion of nickel species, and strong interactions between active phase and support. The catalytic activity of the prepared catalysts was also dependent on the conditions of catalytic test, as the results obtained at temperature 550°C for temperature-programmed and isothermal runs differed. This was indicating that some structural changes in the prepared materials occurred during temperature-programmed catalytic tests, e.g. the formation of inactive spinel phase, which resulted in lower conversions registered at 550°C for temperature-programmed tests than the values observed during isothermal runs at the same temperature. All catalysts exhibited the excess of CO in the products of the reaction, suggesting the occurrence of RWGS. The lowest activity was exhibited by the sample into which nickel was introduced into brucite-like layers. However, this catalyst was loaded with relatively low amount of nickel, and thus this method of nickel introduction may result in a very active catalyst when higher amount of Ni²⁺ species will be introduced into hydrotalcite layers. The highest activity per gram of active material was shown by catalyst loaded with only 0.8wt.% of Ni and prepared via adsorption method. Such high activity, comparable to samples HNI-IMP and HNI-CP loaded with ca. 7wt.%Ni, may be attributed to the formation of small crystallites or aggregates of nickel oxide on catalyst surface. Therefore, the adsorption technique may be used to produce highly active catalyst with very low nickel content, which is very beneficial from the economic standpoint.

All catalysts showed stable performance in DRM reaction at 550°C carried out for 5h. Moreover, all catalysts showed considerable activity at such low temperature, clearly indicating that Ni-containing, hydrotalcite-derived materials are promising catalysts for dry refroming reaction.

9 The effect of nickel content in brucite-like layers

The Ni/Mg/Al and Ni/Al hydrotalcite-like materials with nickel species present in the brucite-like layers have been extensively studied as catalysts precursors for DRM reaction over last 30 years (Chapter 5.5.1, Table 5.8). Recently a number of new publications regarding these type of materials have been published (years 2014-2016) [103, 120, 121, 125, 128, 130-132]. The reported research was focused mainly on the materials with either relatively low (below 20 wt.%) [103, 120, 123, 124, 129, 130] or high (above 50 wt.%) [121, 122, 131, 132] content of nickel. Materials with fixed values of M²⁺/M³⁺ and Ni²⁺/Mg²⁺ molar ratios have also been tested [103, 119, 128-134]. The activity of a wide range of hydrotalcite-derived materials with a varied content of nickel in brucite like layers has not yet been reported. Thus, the studies presented in this Chapter were focused on filling this gap.

Hydrotalcite-like materials were synthesized by co-precipitation at constant pH. All synthesized materials had a fixed value of M²⁺/M³⁺ molar ratio. The parameter which varied was Ni²⁺/Mg²⁺. Nickel cations, which were introduced into brucite-like layers, substituted 0, 5, 15, 25, 50, 70 or 100% of magnesium cations, respectively, giving eight materials with varied nickel content. This Chapter presents the results of physicochemical characterization of the prepared hydrotalcite-derived catalysts and their catalytic evaluation towards dry reforming of methane reaction.

9.1 Physicochemical features of the hydrotalcite precursors and the derived catalysts

9.1.1 XRD analysis of synthesized hydrotalcites and calcined materials

The XRD diffractograms acquired for different prepared hydrotalcites are presented in Fig. 9.1 A. All materials exhibited reflections at 20 ca. 11.5, 23.5, and 35°, originating from diffraction of X-rays on (003), (006) and (009) planes which are typical for 3R rhombohedral layered structure [185, 186, 193]. Irrespective of Ni content, no additional phases were observed, pointing to the successful incorporation of nickel cations into the brucite-like layers. The parameter *a* of hydrotalcite unit cell was equal to 3.06Å (Table 9.1), indicating no structural changes with the incorporation of different amounts of nickel. The values of the *c* parameter of unit cell (Table 9.1), indicated the presence of carbonate anions, and possibly nitrate anions between hydrotalcite layers [185]. The intensity of the reflections arising from hydrotalcite structure was decreasing with the increasing nickel content, pointing to a decrease in crystallinity of hydrotalcite-like materials with increasing Ni loading.



Fig. 9.1 The XRD diffractograms registered for: (A) freshly prepared hydrotalcites, (B) calcined materials; ○ hydrotalcite, ■ MgO periclase-like structure of mixed oxides; ■ NiO

The XRD patterns of calcined catalysts, shown in Fig. 9.1 B, exhibited two main reflections at around 42.5 and 63° 20, which may be assigned to periclase-like structure of Mg(Ni,Al)O mixed oxides [193]. This is typical for the thermal decomposition of hydrotalcite-like materials occurring upon calcination. The intensity of the reflection at 20 equal to 35° was increasing with the increasing nickel content, and was shifted to a value of 37° 20 for sample HNi100. Such shift was expected, as with the decreasing content of magnesium in the Mg(Ni,Al)O oxides, the synthesized mixed oxides were forming structure of NiO. No additional phase was observed for the calcined materials, indicating that calcination temperature was insufficient to cause the formation of phases inactive in DRM, such as NiAl₂O₄ spinel phase.

Sample	Unit cell parameter <i>a</i> (Å)	Unit cell parameter <i>c</i> (Å)	c'=c/3 (Å)	Anions between brucite layers
HNi100	3.06	23.28	7.76	CO_3^{2-} and NO_3^{-}
HNi75	3.06	23.31	7.77	CO_3^{2-} and NO_3^{-}
HNi50	3.06	23.40	7.80	CO_3^{2-} and NO_3^{-}
HNi25	3.06	23.43	7.81	CO_3^{2-} and NO_3^{-}
HNi15	3.06	23.52	7.84	CO_3^{2-} and NO_3^{-}
HNi5	3.06	23.52	7.84	CO_3^{2-} and NO_3^{-}
HT-MgAl	3.06	23.52	7.84	CO_3^{2-} and NO_3^{-}

Table 9.1 Unit cell parameters of synthesized hydrotalcites with varied nickel content in brucite-like layers

9.1.2 FTIR experiments

The FTIR spectra recorded for freshly prepared hydrotalcites (Fig. 9.2), also confirmed the successful synthesis of hydrotalcite-like materials. All samples exhibited absorption bands typical for LDHs, which are listed in Table 9.2. The only difference between the samples was the difference in intensity of absorption band at ca. 670cm⁻¹, which was decreasing with the increasing content of nickel. As reported by Cavani et al. [185], carbonate anions in a symmetric environment are characterized by three IR active absorption bands observed at 1350-1380 cm⁻¹, 850-880cm⁻¹ and 670-690cm⁻¹. The observed decrease of intensity of the band at 670cm⁻¹ was thus most probably caused by lowering the symmetry, thus suggesting different interactions of carbonate anions and brucite-like layers with the increasing nickel content. Moreover, with the increasing magnesium content the intensity of absorption band at 1650cm⁻¹ increased, suggesting higher content of interlayer water for the samples with low content of nickel.

Absorption band (cm ⁻¹)	Band assignment
3550	H-bonded OH groups in brucite-like layers and interlayer water
3000	Stretching vibration of interlayer hydrogen bonding with $\text{CO}_3^{2\text{-}}$
1650	Bending vibration of interlayer water
1376	Asymmetric stretching vibration of NO ₃ ⁻ located between layers
1370	Stretching vibration of CO ₃ ²⁻
870	Out-of-plane vibration of CO ₃ ²⁻
450-700	M-OH stretching and M-O-M bending vibrations

Table 9.2 The assignment of absorption bands in FTIR spectra of hydrotalcite-like materials [128, 189, 247]



Fig. 9.2 FTIR spectra recorded for freshly synthesized hydrotalcites with different content of nickel in brucite-like layers

9.1.3 Elemental analysis

The results of elemental analysis performed by ICP-MS technique are presented in Table 9.3. The obtained results stay in line with XRD analysis, as nominal values of M^{2+}/M^{3+} and Ni^{2+}/Mg^{2+} were very close to the real ones, pointing to the formation of only hydrotalcite-like material with a desired Ni^{2+}/Mg^{2+} molar ratio. The content of nickel varied from ca. 3wt.% for sample HNi5 to around 59 wt.% for sample HNi100.

Sample	Ni (wt.%) ¹⁾	Mg (wt.%) ¹⁾	Al (wt.%) ¹⁾	Ni ²⁺ /Mg ^{2+ 2)}	M ²⁺ /M ^{I3+ 2)}
HNi100	58.66	-	8.92	-	3.02 (3.0)
HNi75	49.10	6.57	10.9	3.09 (3.0)	2.74 (3.0)
HNi50	36.59	14.79	11.07	1.02 (1.0)	3.00 (3.0)
HNi25	19.57	23.85	11.76	0.34 (0.33)	3.02 (3.0)
HNi15	12.27	30.96	13.23	0.16 (0.18)	3.02 (3.0)
HNi5	3.52	32.68	12.84	0.04 (0.05)	2.95 (3.0)
HT-MgAl	-	35.39	13.19	-	2.98 (3.0)

Table 9.3 The chemical composition of hydrotalcite-derived catalysts with nickel cations in brucite-like layers

¹⁾ determined by ICP-MS technique

²⁾ nominal values are given in parenthesis

9.1.4 Texture of the prepared catalysts

The low temperature N₂ sorption experiments showed that all samples exhibited type IV isotherm, which is characteristic for mesoporous materials. Interestingly, the shape of hysteresis loop, which indicates shapes of pores, changed with the nickel content. The catalysts with high content of nickel (HNi100, HNi75, HNi50 and HNi25) exhibited the H2 hysteresis loop, indicating the presence of cylindrical channel pores with nonuniform size and shape. On the other hand, samples HNi15 and HNi5 (with low content of nickel) exhibited H3 hysteresis loop, indicating the slit shaped pores with nonuniform size and shape [248, 249].

The character of pores and distribution of pore size changed with the increasing nickel content, pointing that substituting magnesium cations by Ni²⁺ influences the texture properties of hydrotalcite-derived mixed oxides.

The values of specific surface area, S_{BET} , of nickel containing hydrotalcites, derived from the corresponding N₂ adsorption isotherms through the application of the BET method, ranged between 120 and 190 m²/g (Table 9.4) and were typical for such materials. For the samples, which were obtained by exchanging 25, 50, 75 or 100% of magnesium cations by Ni²⁺, the values of textural parameters were in the same range. The increase in S_{BET} and V_{tot} was observed for HNi15 and HNi5 samples. This was most probably caused by some structural rearrangements, as confirmed by the analysis of the shape of isotherms and hysteresis loops (Fig. 9.3).

Sample	S _{BET} (m²/g)	V _{tot} (cm³/g)	Mean pore diameter (nm)
HNi100	122	0.61	20
HNi75	127	0.29	9
HNi50	126	0.35	11
HNi25	114	0.41	14
HNi15	187	1.45	31
HNi5	166	0.74	18
HT-MgAl	95	0.87	35

Table 9.4 The values of textural parameters obtained for hydrotalcite-derived catalysts with nickel in brucite-like layers



Fig. 9.3 The N₂ adsorption/desorption isotherms registered for hydrotalcite-derived mixed oxides and the corresponding distribution of pores

9.1.5 Reducibility of hydrotalcite-derived mixed oxides

H₂-TPR profiles of the prepared catalysts are presented in Fig. 9.4. In general, all catalysts showed one wide asymmetric reduction peak arising from the reduction of nickel oxide. The maximum temperature of reduction (T_{max}) was shifted to higher temperatures with the decreasing nickel content (with the exception of sample HNi5). The nickel loading influenced both the shape and T_{max} of the reduction peak. It was reported in literature, that nickel oxide forms MgO-NiO solid solution with magnesia in all molar ratios, which increases the interactions between active material and support [93, 233, 255]. Moreover, as reported by Hu [255] and Daza et al. [236], reduction of Ni²⁺ is only possible in Ni-O-Ni and not possible in Ni-O-Mg species. With the decreasing amount of nickel, the dilution of Ni in the solid solution of oxides increases, and thus the probability of finding Ni-O-Ni species is lower, and, in consequence, the reduction of NiO occurs at higher temperatures. Moreover, as Ni species needed to be extracted from the Mg(Ni,Al)O framework in order to form metallic nickel crystallites on the support surface, it may be stated that with the decreasing content of nickel the nickel crystallite size was decreasing and dispersion of Ni species was increasing. In case of HNi100 sample an additional low intensity peak was observed at 420°C which is related to the reduction of surface nickel oxide [256, 257]. The lack of this reduction peak in the case of other studied catalysts may be explained by the interactions of NiO with magnesia.



Fig. 9.4 The H₂-TPR profiles of calcined hydrotalcite-derived materials with nickel introduced into brucite-like layers

9.1.6 Basicity of hydrotalcite-derived materials containing nickel in brucite-like layers

The basicity of the catalysts is an important factor in DRM reaction, as CO₂ adsorption is facilitated on the basic sites. Thus, high basicity of the catalyst can influence its activity, as shown e.g. by high concentration of strong basic sites enhancing catalytic activity of samples HNi-IMP and HNi-CP in comparison to other catalysts described in Chapter 8. Moreover, high basicity can help to oxidize carbon deposits formed during DRM process via Boudouard reaction. On the other hand, acidic catalysts favour the formation of carbon deposits. As total basicity of calcined and reduced hydrotalcite-derived materials is influenced by the composition of brucite-like layers, the CO₂-TPD experiments were applied to establish the effect of nickel content on basic properties of HTs-based catalysts. The obtained CO₂-TPD desorption profiles are depicted in Fig. 9.5. All calcined catalysts (Fig. 9.5 A) evidence a wide and asymmetric CO₂ desorption peak, centred at temperatures around 130-150°C, together with two shoulders at ca. 180-200 and 270-300°C. The profiles correspond to adsorption on weak (100-150°C), medium (ca. 190°C) and strong (ca. 280°C) basic sites of hydrotalcite-derived mixed oxides.

The total basicity was calculated by means of the integration of the overall desorption profile, which was deconvoluted into three Gaussian contributions corresponding to each type of basic sites (Table 9.6). For the calcined catalysts, the total basicity decreased with the increasing Ni content. This may be ascribed to the decreasing MgO content in the mixed oxide phase, since its presence may favour CO₂ adsorption, e.g. through the enhanced formation of stable carbonate species.

	Calcined samples			Reduced samples				
Sample	W ¹⁾	M ²⁾	S ³⁾	Total	W ¹⁾	M ²⁾	S ³⁾	Total
	(%)	(%)	(%)	(µmol/g)	(%)	(%)	(%)	(µmol/g)
HNi100	27	42	31	69	49	45	6	37
HNi75	21	35	45	138	35	59	7	51
HNi50	22	35	42	162	42	43	15	83
HNi25	24	37	39	213	31	27	43	104
HNi15	19	29	52	249	25	44	31	82
HNi5	18	32	50	250	35	57	8	60
HT-MgAl	16	30	54	231	30	58	12	93

Table 9.5 The integration and deconvolution of CO_2 -TPD profiles for the calcined and the reduced catalysts: W (weak), M (medium-strength) and S (strong) basic sites, and total basicity (μ mol CO_2/g)

¹⁾percentage of weak basic sites; desorption peak T<200°C

²⁾percentage of medium strength basic sites; desorption peak 200°C<T<300°C

³⁾percentage of strong basic sites; desorption peak T>300°C



Fig. 9.5 CO₂-TPD profiles registered for: calcined (A) and reduced (B) hydrotalcite-derived catalysts with nickel introduced into brucite-like layers

The distribution of weak, medium and strong basic sites remained similar for all calcined materials, with a higher contribution of strong basic sites, as could be expected from CO₂ adsorption on a mixed oxide phase. An additional desorption peak was observed above 600°C (results not shown), which can be attributed to the completion of dehydroxylation process and decomposition of carbonate anions formed upon CO₂ adsorption [253].

The CO₂-adsorption capacity of the hydrotalcite-derived catalysts changed dramatically upon their reduction under 5% H₂/Ar at 900°C. The total basicity of the catalysts after reduction decreased 2-4 times with respect to the calcined materials and strongly depended on the nickel content (Table 9.5). Moreover, the distribution of basic sites changed, especially where strong basic sites are considered. The contribution of these sites to total basicity increased with decreasing Ni content, reaching a maximum of 43% for HNi25 catalyst, and then decreased for HNi15 and HNi5. As it was discussed in Chapter 8.4.2, the highest conversions of CH₄ and CO₂ were observed for catalysts with the highest content of strong basic sites. Thus, one can expect high activity in DRM for sample HNi25. Moreover, a shift to higher desorption temperatures was observed for the peaks corresponding to medium and strong basic sites. The increasing presence of MgO species with the decreasing Ni-content may partially explain these facts. However, different types of CO₂ chemisorption on Ni(111), Ni(100) and Ni(110) surfaces was reported in literature [258]. The presence of different Ni planes may be controlled by crystal size and, ultimately, by Ni content, and thus may as well contribute to the dissimilarities observed in terms of basicity among different reduced catalysts.

9.1.7 TEM and SEM analysis of calcined and reduced catalysts

Electron microscopies (SEM and TEM) were used to study the morphology of selected calcined and reduced catalysts.



Fig. 9.6 The SEM micrographs registered for calcined HNi100 (A), calcined HNi25 (B), reduced HNi100 (C) and reduced HNi25 (D) catalysts

The SEM images recorded for calcined and reduced catalysts are presented in Fig. 9.6. Upon calcination of hydrotalcites at moderate temperatures (500-600°C), the layered structure

collapse and mixed oxides with nano-sphere morphology are formed. Most commonly these mixed oxides exhibit plate/flake-like shaped structure. The shape of mixed oxides nano-particles can be influenced by the calcination conditions, aging etc [124]. The recorded images showed that the obtained materials were composed of irregular particles of flake-like shape with sizes between 2-50µm. These particles were composed of a group of layers characteristic for the layered aggregates of periclase phase.



Fig. 9.7 TEM micrographs registered for calcined catalysts: HNi100 (A), HNi75 (B), HNi50 (C), HNi25 (D), Hni15 (E) and HNi5 (F)



Fig. 9.8 TEM images and the corresponding histograms of nickel particle size distribution registered for the reduced catalysts: HNi100 (A), HNi75 (B), HNi50 (C), HNi25 (D), HNi15 (E) and HNi5 (F)

The TEM images for the calcined materials (Fig. 9.7) also confirmed the presence of nanostructure arrays of flake-like particles. The size of the observed aggregates was influenced by nickel content, and was decreasing with increasing Ni loading. Moreover, no separate Ni-phase was distinguished, in agreement with XRD analysis (Fig. 9.1B), indicating that Ni oxides were present in the form of a mixed oxide solution (periclase) together with Mg and Al oxides. Furthermore, the lamellar structure of hydrotalcites was well conserved in the materials after calcination. The presence of carbonates, probably formed upon the-exposure of the calcined catalysts to ambient air, was confirmed by the existence of crystalline planes of average planar distance around 5-6Å. The electron microscopies confirmed additionally that the materials were homogenous and well crystallized. The EDX analysis performed in various zones of the materials together with TEM and SEM experiments revealed a uniform materials composition.

	TEM analysis	XRD analysis				
Sample	Ni particle size ¹⁾ (nm)	Ni particle size ²⁾ (nm)	Relative intensity of Ni(200) ³⁾ (%)			
HNi100	19	20	46.5			
HNi75	15	16	37.7			
HNi50	12	9	31.7			
HNi25	7	6	30.1			
HNi15	11	9	26.7			
HNi5	6	5	20.3			

Table 9.6 The Ni crystallite size calculated basing on TEM and XRD analysis and relative intensity of Ni(200) reflection with respect to Ni(111) reflection

 $^{\mbox{\tiny 1)}}$ values calculated by analysis of TEM images

²⁾ values estimated using Scherrer equation

³⁾ values calculated by the intensity of Ni(200)/Ni(111)

After reduction in 5%H₂ in Ar at 900°C for 1h, some morphological changes become visible in SEM images. In general, on the surface of flake-like shaped particles, smaller aggregates were located (Fig. 9.6 C and D). The coverage of the support surface and the amount of such small particles was increasing with the decreasing content of nickel. As confirmed by EDX and XRD analysis, the calcined materials contained only one phase. Thus during reduction of the catalysts, the surface and bulk NiO was segregated from the periclase structure of Mg(Ni,Al)O oxides, causing the destruction of the periclase surface phase and the formation of cauliflower-like aggregates on the surface.

TEM micrographs obtained for the reduced catalysts and the distribution of nickel particles are shown in Fig 9.8. In order to determine an average particle size, between 300-400 particles were measured. In all micrographs dark spots were observed, which were ascribed to the

Ni^o particles, with interplanar spacing of 2Å, dispersed on the support, as confirmed by the diffraction analysis. All catalysts exhibited homogenous distribution of nickel particles. The size of nickel particles was dependent on the nickel loading, and as expected, decreased with the decreasing nickel content (Table 9.6). For the whole set of hydrotalcite-derived catalysts Ni particle size decreased from 19nm (sample HNi100) to 5nm (sample HNi5).

9.1.8 XRD analysis of reduced catalysts

The XRD patterns of the catalysts after activation in 5%H₂/Ar are presented in Fig. 9.9. All catalysts showed reflections at 20 equal to ca. 44, 51 and 76° characteristic for cubic metallic nickel structure (ICOD 01-087-0712). The intensity of these reflections was increasing with increasing content of nickel, clearly suggesting the increase of nickel crystallite size with the increasing loading of Ni, in agreement with TEM results. The estimated values of Ni crystallite size, calculated using the position of Ni(200) reflection and Scherrer equation, are presented in Table 9.6. Basing on the obtained XRD patterns of the reduced catalysts relative intensity of Ni(200) reflection with respect to Ni(111) reflection was also calculated. It has been reported in literature [73] that the side reactions accompanying DRM, i.e. carbon-forming reactions, are structure sensitive and tend to occur on Ni(200) and Ni(220), rather than Ni(111) planes. The calculated values of this parameter were increasing with the increasing Ni content, suggesting that carbon forming reactions would proceed more easily on the catalysts with high content of nickel (HNi100, HNi75, HNi50), as these samples exhibited large size of Ni crystals and relatively high intensity of Ni(200) reflection.



Fig. 9.9 The XRD diffractograms registered for catalysts reduced in $5\%H_2/Ar$ at $900^{\circ}C$; Detected phases: •metallic nickel, \blacksquare Mg(Ni,Al)O with periclase-like structure, \blacktriangle NiAl₂O₄, \triangle MgNi₃;

The reflections characteristic for periclase-like structure of mixed oxides (20 equal to ca. 43 and 63°) are also present in Fig.9.9. Contrary to the reflections originating from metallic nickel, the intensity of these reflections was decreasing with the increasing nickel content and they were absent for sample HNi100. Upon reduction nickel species are extracted from the framework of periclase-like mixed oxides. The obtained results suggest that with the increasing nickel content, the crystallinity of mixed oxide phase decreases.

Additional phases were also observed for the reduced catalysts. Samples HNi5 and HNi15 showed the presence of $NiAl_2O_4$ spinel phase. Moreover, MgNi₃ phase was observed for reduced HNi5, HNi15 and HNi25 catalysts.

9.2 Activity, selectivity and stability of the hydrotalcite-derived catalysts during DRM runs

Figures 9.10 A and B depict the CH₄ and CO₂ conversions measured during the DRM experiments performed at 550°C over different hydrotalcite-derived catalysts and, for comparison, Ni/Al₂O₃ catalyst (10 wt.%). CH₄ conversion was increasing with the increasing loading of nickel, with the exception of sample HNi75, which showed the highest conversion of methane after ca. 70 minutes of reaction. The activity towards methane conversion formed a sequence: HNi75 > HNi100 > HNi50 > HNi25 >> HNi15 \approx Ni/Al₂O₃ > HNi5. No decrease in catalytic activity towards CH₄ conversion was observed during 5h TOS.

CO₂ conversions did not depend so strongly on the nickel content, as all catalysts showed very similar activity towards DRM reaction. However, the significant decrease in CO₂ conversion was observed during first 60-80 minutes of the catalytic runs till CO₂ conversions reached stable values (for HNi100, HNi75, HNi50 and HNi25 catalysts). This may have been caused by the deposition of catalytic coke on the catalysts surface, which influenced their activity. The highest CO₂ conversion was measured for HNi25 sample.

CH₄ conversions were higher than CO₂ conversions for samples HNi75 and HNi100. The opposite tendency was observed for HNi5, HNi15 and Ni/Al₂O₃ catalysts and for sample HNi25 during first 60-80 minutes of the reaction. This indicates a strong influence of different side reactions. Higher conversions of CH₄ with respect to CO₂ were most probably caused by the occurrence of CH₄ decomposition. On the other hand, CO₂ conversions higher than those of CH₄, suggest the occurrence of reverse water gas shift reaction (RWGS). These results stay in line with the registered values of H₂/CO molar ratio, as the excess of H₂ or CO was observed in the products of the reaction, respectively.



Fig. 9.10 The results of catalytic tests in DRM reaction carried out at 550°C over hydrotalcite-derived catalysts:
 (A) CH₄ conversion, (B) CO₂ conversion, (C) H₂/CO molar ratio;
 GHSV=2000h⁻¹, CH₄/CO₂/Ar=1/1/8, total flow 100cm³/min

The performance of the tested catalysts in DRM reaction may be divided into two groups. The samples with high and medium content of nickel, obtained by substitution of 100, 75, 50 or 25% of Mg²⁺ by Ni²⁺, showed higher conversions of CH₄ than those of carbon dioxide, and thus the excess of hydrogen in the products of the reaction was registered (Fig. 9.10 C). The ratio of H₂/CO was strongly affected by the nickel content, and the excess of H₂ in the obtained products was more evident with the increasing nickel content. On the other hand, the catalysts with low loading of nickel (HNi5 and HNi15) exhibited higher conversions of CO₂ than of CH₄, as well as the excess of carbon monoxide in the products of the reaction. Sample HNi5 turned out to be the least active of all testes catalysts. Such high differences in the distribution of the obtained products strongly suggest the occurrence of side reactions.

The reference catalyst, 10wt.% Ni/Al₂O₃, showed very similar performance to sample HNi15 in terms of methane conversion. However, a constant decrease was observed for the former catalyst, pointing to its deactivation. CO₂ conversion registered for the Ni/Al₂O₃ were similar to that observed for HNi100 sample, after ca. 150 min TOS. However, the CO₂ conversions of most tested catalysts were at a similar level. The comparison of the performance of the reference catalyst with the hydrotalcite-derived ones, showed the advantages of the latter. Higher activity of samples HNi100, HNi75, HNi50 and HNi25 may be explained by the higher nickel loading.

9.2.1 The characterization of the spent catalysts

The XRD patterns recorded for the spent catalysts after 5h DRM reaction are depicted in Fig. 9.11. All catalysts exhibited reflections originating from metallic nickel phase (ICOD 01-087-0712) and Mg(Ni,Al)O nano mixed oxides with periclase like structure (reflections at 20: 43, 62.5°; ICOD 01-087-0652), with the exception of sample HNi100, which showed the presence of cubic Al₂O₃ (reflections at 20: 37, 45 and 68°; ICOD 00-001-1308). The presence of alumina phase indicates, that upon DRM reaction nickel species are separated from the Ni(Al)O phase of periclase forming in this way phases of metallic nickel and Al₂O₃ in case of sample HNi100. The other samples still exhibited periclase-like phase of mixed oxides, pointing to a stabilization of mixed oxide structure in the presence of magnesium. Moreover, the intensity and width of the reflections originating from the mixed oxide phase were decreasing with the increasing nickel content, in agreement with average values of Mg(Ni,Al)O size (Table 9.7). The opposite trend was observed for the reflections arising from Ni⁰ structure. It is expected that with the increasing content of nickel, the Ni⁰ crystallite size increases and the size of Mg(Ni,AlO) mixed oxides crystallites decreases. This was confirmed by the estimation of Ni⁰ and mixed-oxides crystallite size basing on Scherrer equation (Table 9.7). Crystal sizes for Ni⁰ practically corresponded to the mean particle sizes evidenced by the corresponding TEM-derived histograms (Fig. 9.12), pointing to no obvious sintering of the Ni-phase occurring at 550°C during 5h-isothermal experiments.



Fig. 9.11 The XRD diffractograms registered for the catalysts after DRM reaction at 550°C; Detected phases: \bullet metallic nickel, \blacksquare periclase-like mixed oxides, \blacktriangle NiAl₂O₄, \triangle MgNi₃, \blacktriangledown graphitic carbon, ∇ Al₂O₃

In case of almost all catalysts (with the exception of HT-5Ni), an additional reflection at 20 ca. 26°, originating from the graphitic carbon, was observed. The intensity of this reflection was decreasing with the decreasing content of nickel, further confirming the hypothesis that large Ni particles are more active towards direct methane decomposition, which leads to the formation of carbon deposits [73, 259, 260]. The occurrence of CH₄ decomposition also explains the excess of H₂ in the products of DRM reaction observed for catalysts with high Ni loadings (Fig 9.10 C).

		XRD analysis	TEM analysis			
Sample	Mg(Ni,Al)O crystallite size ²⁾ (nm)	Ni crystallite size -reduced ¹⁾ (nm)	Ni crystallite size-spent ²⁾ (nm)	Ni crystallite size-reduced ¹⁾ (nm)	Ni crystallite size-spent ²⁾ (nm)	
HNi100	np	20	18	19	21	
HNi75	4	16	14	15	16	
HNi50	5	9	13	12	14	
HNi25	5	6	11	7	13	
HNi15	7	9	6	11	8	
HNi5	6	5	4	6	6	

Table 9.7 The nickel and periclase-like mixed oxides crystallite sizes estimated for the reduced and spent catalysts after 5h DRM reaction at 550°C, based on XRD and TEM analysis

¹⁾ estimated for the reduced catalysts

²⁾ estimated for the catalysts after 5h DRM reaction at 550°C



Fig. 9.12 TEM images and corresponding distribution of nickel particles registered for the spent catalysts after 5h DRM reaction at 550°C: (A) HNi100, (B) HNi75, (C) HNi50, (D) HNi25, (E) HNI15 and (F) HNi5
For the two catalysts prepared with the lowest Ni-content, HNi15 and HNi5, the presence of additional reflections at 20: 42, 49 and 71.5° points to the presence of a magnesium nickel alloy MgNi₃ (ICOD 04-016-6336), formed upon DRM reaction. Moreover, some reflections corresponding to an hydrotalcite-like structure of meixnerite (20: 11, 23 and 35°; ICOD 00-050-1684) were registered, suggesting that over HNi15 and HNi5 catalysts the RWGS reaction, resulting in the production of water and CO, may be especially activated, causing the reconstruction of the layered structure due to the memory effect. These results are in good agreement with low H_2 /CO ratios measured for HNi15 and HNi5 catalysts during DRM reaction (Fig. 9.10 C).

The TEM (Fig. 9.12) and SEM images (Fig. 9.13) recorded for the spent catalysts clearly evidence the changes in samples morphology and the formation of carbon structures. Whisker-like carbon filaments, i.e. fishbone type [76], having a diameter around 13-80nm, were visible in TEM and SEM micrographs acquired for all catalysts. The diameter and amount of these whisker-shaped multiwall carbon nano-tubes were decreasing with the decreasing nickel loading.



Fig. 9.13 SEM micrographs registered for: (A) HNi100 (x10 000), (B) HNi75 (x50 000), (C) HNi50 (x50 000) and (D) HNi15 (x10 000)

On the top of carbon whiskers Ni particles were observed. Such effect has already been reported in literature [76, 125]. It is considered that the carbon atoms originating from dissociative adsorption of CH_4 on nickel crystallites may dissolve in the nickel crystallites, and then diffuse through nickel, and subsequently nucleate and precipitate at the rear end of the crystallite. This leads to the formation of carbon multiwall nanotubes of whisker-like shape and, as a result, nickel crystallite is lifted from the catalyst surface.

Fig. 9.12 additionally presents the distribution of Ni particle size. For all catalysts the most frequent values of Ni particle size are in agreement with the ones estimated by XRD analysis (Table 9.7). It is important to stress that with the increasing content of nickel, the distribution of particle size became wider, and in case of samples HNi100, HNi75 and HNi50 a wide range of nickel crystallite sizes was registered. Nevertheless, the mean values of Ni⁰ phase, as compared for to those observed for the reduced catalysts (Fig. 9.8), did not directly evidence sintering of active phase. However, the distributions of nickel particle sizes were much wider for the spent catalysts, which may have been the result of sintering. As Ni particles were lifted from the support by carbon whiskers, the interaction between active material and support grew weaker and, as a result, sintering of nickel particles may have been favoured. The TEM micrographs also confirmed the presence of amorphous carbonaceous species on the catalysts surface.

The amount of deposited carbon was measured by a series of thermogravimetric oxidation experiments after 5h reactions at 550°C. Fig. 9.14 shows the mass loss and its derivative, measured as a function of temperature. Carbon formed during DRM reaction oxidizes in the temperature range of 450-650°C. The DTG profiles evidence either a single wide peak or two separate exothermic peaks located at ca. 580 and 610°C (for HNi100 catalyst), pointing to the formation of at least two types of carbonaceous materials of different thermal stability towards oxidation. The position of these two overlapping peaks is shifted to lower temperatures with the decreasing Ni content, pointing to the influence of Ni particle/crystal size not only on the amount (Table 9.8), but also on the thermal stability of the formed on the catalysts surface upon DRM reaction, especially for the samples with high Ni loading, the catalytic activity of the tested materials was not affected, as no decrease in CH₄ and CO₂ conversion (after ca. 100 min TOS) was observed.

Tsyganok et al. [261] observed three regions of oxidation in TG analysis of hydrotalcitederived nickel-containing catalysts: (i) at 250-300°C associated with desorption of adsorbed water, CO_2 and easily oxidized carbonaceous species, (ii) at 410-450°C associated with oxidation of metallic nickel supported on the catalyst surface, and (iii) at 480-600°C associated with oxidation of carbon deposits (two exothermic peaks). According to literature [103, 147], the carbonaceous species of the first temperature region are amorphous and may participate in the syngas formation via gasification with CO₂ or H₂O, while the carbon deposits of the higher temperature region (iii) are mainly inactive graphitic coke which does not affect the DRM activity. On the other hand, Zhang et al. [147] reported that carbonaceous species of graphitic form that were oxidized at temperatures higher than 600°C may also participate in CO formation. As in DTG profiles mainly two peaks in the temperature region of 450-650°C were observed, it may be stated that the graphitic coke formed during 5h DRM reaction at 550°C was not poisonous.



Fig. 9.14 The TGA profiles for the temperature programmed oxidation of the carbon deposits in the spent catalysts: (A) weight loss, (B) dTGA signal vs. temperature

Sample	Mass loss (%)	Amount of deposited coke (mg/g _{cat} /h)
HNi100	83.1	0.98
HNi75	76.8	0.66
HNi50	58.8	0.28
HNi25	52.7	0.22
HNi15	54.4	0.24
HNi5	35.8	0.11

Table 9.8 The results of thermogravimetric oxidative analysis of the spent catalysts after 5h DRM reaction at 550°C

The peak observed around 350°C for HNi5 sample may be assigned to the desorption of adsorbed water, i.e. responsible of the regeneration of the hydrotalcite layered-structure, as suggested by XRD pattern of the appropriate catalyst (Fig. 9.11).

The results of low temperature N_2 sorption measurements carried out for the samples after 5h-catalytic tests in DRM at 550°C are presented in Table 9.9. All samples exhibited the decrease in the values of S_{BET} and V_{tot} with respect to the values obtained for the catalysts before reaction. The highest decrease of textural parameters was observed for the catalysts with high Ni loading (HNi100, HNi75 and HNi50), which corresponds to the formation of the highest amount of carbonaceous deposits on catalysts surface, which caused the blockage of pores. These results are in good agreement with XRD and TG results obtained for the spent catalysts. The lowest decrease of textural parameters was observed for sample HNi25, which also showed the highest conversions of CO_2 .

The results of catalytic tests (Fig. 9.10) showed that the catalysts exhibited stable performance, with no decrease of CH_4 and CO_2 conversions during 5h isothermal tests at 550°C. On the other hand, the characterization of the spent catalysts showed that carbon deposits were formed on all samples. The amount and type of these deposits was dependent on the nickel content, and was increasing with the increase of Ni loading. This may be explained by the fact that Ni particles were lifted from the surface of the catalysts by carbon nanotubes, and thus the contact to DRM nickel active centres was not blocked. However, such lifting of nickel particles decreases interactions between active phase and support, which may lead to sintering of Ni species and catalyst deactivation during catalytic runs longer than 5h.

		Before reaction			After reaction			
Sample	S _{BET} (m²/g)	V _{tot} (cm³/g)	Average r _p (nm)	S _{BET} (m²/g)	V _{tot} (cm³/g)	Average r _p (nm)	in S _{BET} (%)	
HNi100	122	0.61	20	58	0.27	18	52	
HNi75	127	0.29	9	67	0.25	17	47	
HNi50	126	0.35	11	73	0.32	15	42	
HNi25	114	0.41	14	99	0.40	14	13	
HNi15	187	1.45	31	125	0.65	21	33	
HNi5	166	0.74	18	137	0.68	20	18	

Table 9.9 Textural properties of the studied catalysts before and after DRM at 500°C for 5h

9.2.2 On the influence of CH₄ decomposition

The results of DRM isothermal catalytic tests at 550°C revealed that the samples with high loadings of Ni led to an excess of H₂ in the products stream and CH₄ conversions higher than those of CO₂, in agreement with thermodynamics (cp. Chapter 7), since CH₄ decomposition is favoured at low temperatures. Moreover, CO₂ conversions for these catalysts were decreasing during ca. first 150 minutes of the reaction. All catalysts (with the exception of HNi5 sample) exhibited the presence of graphitic carbon on the surface, pointing to the occurrence of side carbon-forming reactions, as confirmed by TEM, SEM, TG and XRD experiments. It has been reported in literature [262-264], that hydrotalcite-derived catalysts with high nickel loading in brucite-like layers are

active in methane decomposition. Additionally, Ashok et al. [262] observed that the main product of CH₄ decomposition over Ni/Cu/Al hydrotalcite-derived catalysts was graphitic carbon. In order to check the activation of this key carbon-forming reaction, methane decomposition experiments were performed at 550°C in the presence of different HT-derived catalysts.



Fig. 9.15 CH₄ decomposition over hydrotalcite-derived catalysts with different content of nickel in brucite-like layers; CH₄/Ar=2/8, total flow 100cm³/min, GHSV=2000h⁻¹;

The results of CH₄ decomposition catalytic tests are depicted in Fig. 9.15. Methane conversions registered are generally lower than those measured during the DRM runs. However, all studied catalysts showed considerable activity in direct methane decomposition. The CH₄ conversions followed the same pattern as methane conversions in dry reforming reaction and increased with the increasing loading of Ni. The highest observed conversion was equal to ca. 35% for HNi75 catalyst after approximately 250 minutes. The initial conversions of methane increased with the increasing nickel content. All samples (with the exception of HNi5 and HNi15 catalysts) exhibited during ca. first 70-80 minutes of the reaction an increase in CH₄ conversion, resulting in the formation of carbon deposits on the catalysts surface, as confirmed by XRD experiments (results not shown). This may explain the initial loss of activity towards CO_2 during DRM process over these catalysts. The activity in CH₄ decomposition of HNi15 and HNi5 catalysts was much lower in comparison to other materials, again similarly as in DRM reaction. Sample HNi5 turned out to practically inactive in CH₄ decomposition reaction. Coming back to the results of the physicochemical characterization of the reduced catalysts (TEM Fig. 9.8, XRD Fig. 9.9), increasing Ni content was found to result in larger Ni particle sizes upon reduction under 5%H₂/Ar for 1h. Moreover, with decreasing nickel content the relative intensity of Ni(200) reflection decreased. As previously reported [73, 259, 260, 262], Ni crystal sizes were found to play an important role in carbon

formation through CH₄ decomposition and on the type of carbon deposited on the catalyst surface. The obtained results (Fig. 9.15) further confirm this fact. Thus, the activity of hydrotalcite-derived catalysts towards methane decomposition at low temperatures may be controlled through tailoring of Ni particle/crystal size, which in turn depends on the amount of nickel incorporated in the brucite-like layers of hydrotalcite structure.

The obtained results of CH_4 decomposition showed that this reaction strongly influences the DRM process, when HT-derived catalysts with high nickel content are applied, and is responsible for the obtained H_2/CO molar ratios higher than unity by increasing CH_4 conversions.

9.2.3 On the effect of catalysts basicity on their catalytic performance in DRM

The methane conversion in dry reforming process over the catalysts tested at 550°C was mainly influenced by direct methane decomposition reaction, as discussed in the previous subchapter. On the other hand, the CO₂ conversions of the prepared catalysts were mainly influenced by their basic properties, as illustrated in Fig. 9.16, which depicts average conversions of CH₄, CO₂ and average H₂/CO molar ratios registered during 5h tests at 550°C for different hydrotalcite-based catalysts. It may be observed that the sample HNi25, which exhibited the highest CO₂ conversion, showed also the highest basicity. With respect to other catalysts, sample HNi25 had also the highest amount of strong basic sites, which according to literature, are associated with low coordinated O²⁻ anions [196, 197]. The presence of strong Lewis basic sites facilitates the adsorption of CO₂ and thus may enhance conversion of carbon dioxide and promote oxidation of carbon deposits via Boudouard reaction.



Fig. 9.16 Average conversions of methane (A), carbon dioxide (B) and H₂/CO molar ratio (C) registered during 5h DRM catalytic tests at 550°C as a function of catalysts basicity

The obtained results (Fig. 9.16) clearly indicate that catalytic activity of hydrotalcitederived catalysts with nickel introduced into brucite-like layers of catalyst precursors is a function of basicity. The basicity of the materials, and especially the content of strong basic sites (Table 9.5), influenced the catalyst activity. Basing on the obtained results it can be stated that by exchanging 25% of Mg²⁺ by Ni²⁺ with respect to naturally occurring Mg/Al hydrotalcite, it is possible to obtain a catalyst with the optimal composition for DRM reaction.

9.2.4 On the influence of temperature on catalytic activity of Ni/Mg/Al hydrotalcitederived catalysts

Two catalysts, which showed the highest average conversions of CH₄ and CO₂, samples HNi100 and HNi25, containing ca. 58 and 19 wt.% of Ni, respectively, were selected for isothermal 5h DRM tests at 650 and 750°C. Fig 9.17 presents the evolution of CH₄ and CO₂ conversions, together with the H_2/CO molar ratio at temperatures from 550 to 750°C. For both catalysts activity increased with temperature, due to the endothermic nature of dry methane reforming. For HNi100 catalyst CH₄ conversions were higher than those of CO₂ at all three tested temperatures. However, the difference between CH₄ and CO₂ conversion decreased with temperature. The opposite trend was observed for HNi25 catalyst, which exhibited higher conversions of CO₂ than those of CH₄ at 650 and 750°C. As shown in Fig. 9.17 C, the values of H₂/CO ratio for both catalysts at 550°C were well below the ones predicted by thermodynamics (as discussed in Chapter 7), and decreased with the increasing reaction temperature to finally reach the desired H_2/CO ratios close to 1, at 650-750°C. Both CH₄ conversions and H₂/CO ratios are considerably higher for HNi100 than HNi25 catalyst, pointing to a strong influence of Ni-content on the activation of H₂-producing reactions at low temperatures, i.e. CH₄ decomposition. According to thermodynamic calculations (cp. Chapter 7), carbon-forming reactions, such as direct methane decomposition, are favoured at low temperatures i.e. 550°C. Methane decomposition is thus bound to happen over a catalyst with high Ni content, as reported in Chapter 9.2.2. However, the influence of this reaction seems to be decreasing with the increase of temperature, as it is reflected with decreasing H_2/CO ratios. On the other hand, it seems that HNi25 catalyst was mostly affected by the occurrence of RWGS reaction, which resulted in H_2/CO molar ratios below unity at 650 and 750°C.

The equilibrium conversions of CH_4 and CO_2 in the tested reaction conditions are equal to ca. 64 and 43%, respectively, and equilibrium value of H_2/CO ratio is equal to ca. 3.5 at 550°C. In case of both studied catalysts CH_4 conversions were much lower than the ones predicted by thermodynamics, suggesting that although CH_4 decomposition reaction was well developed at 550°C, the catalysts strongly influenced the selectivity of the process towards dry reforming.



Fig. 9.17 The results of DRM catalytic tests over HNi100 and HNi25 catalysts carried out at 550, 650 and 750°C: (A) average CH₄ conversion, (B) average CO₂ conversion and (C) average H₂/CO molar ratios registered during 5h TOS as a function of temperature; CH₄/CO₂/Ar=1/1/8, total flow 100cm³/min, GHSV=20000h⁻¹

The average values of CH₄ conversions were approaching equilibrium ones with increase in temperature. CO₂ conversions reached thermodynamic equilibrium values at 650 and 750°C for

both catalysts. The experimental average values of CO₂ conversion higher than equilibrium ones presented in Fig. 9.17B may be explained by the fact that they were within experimental error range or may have arisen from the fact that thermodynamic analysis was performed considering the closed system and not a flow reactor.

9.2.5 On the effect of feed gas composition

The two selected catalysts were also tested at 550 and 750°C in DRM reaction with different feed gas compositions. The experiments with the excess of methane, excess of CO_2 and lower dilution with Ar (with respect to catalytic tests reported in the previous chapters) were performed and the results of these tests are summarized in Table 9.10 and presented in Fig. 9.18, 9.19 and 9.20 for sample HNi100 tested at 550°C and HNi25 tested at 550 and 750°C, respectively.

Sample/ Temperature	Feed gas CH₄/CO₂/Ar	Average ¹⁾ CH ₄ conversion (%)	Average ¹⁾ CO ₂ conversion (%)	Average ¹⁾ H ₂ /CO molar ratio (-)
	1/1/8	52.0	38.6	1.58
	1.5/1/7.5	45.8	40.4	2.14
HN1100/550 C	1/1.5/7.5	52.7	30.8	1.25
	1.5/1.5/7	41.8	31.0	1.57
HNi25/550°C	1/1/8	43.5	40.3	1.10
	1.5/1/7.5	37.3	40.0	1.50
	1/1.5/7.5	39.3	30.5	0.81
	1.5/1.5/7	32.0	33.6	0.88
	1/1/8	89.0	91.8	0.93
HNi25/750°C	1.5/1/7.5	77.3	93.8	1.03
	1/1.5/7.5	93.3	76.4	0.80
	1.5/1.5/7	82.9	87.1	0.90

Table 9.10 The average CH_4 , CO_2 conversions and H_2/CO ratios registered over 5h DRM catalytic tests over HNi100 and HNi25 catalysts with different feed gas compositions

 $^{1)}$ Average values of CH $_4$ and CO $_2$ conversions registered during 5h TOS DRM catalytic tests at 550 and 750°C with different feed gas compositions

According to thermodynamics, the excess of methane in the feed gas should result in decreased conversion of CH_4 and increased CO_2 conversion and higher H_2/CO ratios. Moreover, the carbon-forming reactions should be favoured with respect to equimolar CH_4/CO_2 feed gas composition. On the other hand, the opposite trend should be expected in catalytic tests in the excess of CO_2 , i.e. increased CH_4 conversion, decreased CO_2 conversion, H_2/CO molar ratios close to unity and decreased formation of carbon deposits at temperatures above 600°C, as discussed in Chapter 7.



Fig. 9.18 The results of catalytic tests carried out over HNi100 catalyst in DRM reaction at 550°C for different compositions of feed gas: (A) CH₄ conversion, (B) CO₂ conversion, (C) H₂/CO molar ratio; total flow 100cm³/min, GHSV=20000h⁻¹

The HNi100 catalyst tested at 550°C showed (Fig. 9.18), as expected, increased conversion of CH_4 and CO_2 with the excess of methane and carbon dioxide in feed gas, respectively. The obtained values of H_2/CO ratio also followed trends predicted by thermodynamics. It was expected, that the excess of CO_2 in feed gas will enhance the amount of CH_4 converted to CO and H_2 , resulting in the increase of CH_4 conversion. This observation further confirmed that CO_2 as an mild oxidant had a positive effect on CH_4 conversion. On the other hand, the increase in CH_4/CO_2 feed ratio could increase carbon deposition on the surface of the catalyst as a result of CH_4 decomposition, which stays in line with observed higher values of H_2/CO ratios.

The introduction of both methane and carbon dioxide in the higher amount resulted in the decrease of both conversions by ca. 10%. The observed H_2/CO values were not affected when the CH₄/CO₂/Ar ratios were increased from 1/1/8 to 1.5/1.5/7, and were equal in both cases to ca. 1.6. Thus, the decrease in feed gas dilution by argon had a negative effect on catalyst activity towards CH₄ and CO₂, but did not influence the distribution of the obtained products.

The results of catalytic tests with different feed ratios at 550 and 750°C over HNi25 catalyst are presented in Fig. 9.19 and 9.20, respectively. The tests carried out in excess of CH₄ resulted in decreased conversions of methane. However, the test at 550°C showed that CH₄ conversion was increasing with TOS, pointing to enhanced direct CH₄ decomposition. On the other hand, the test at 750°C showed a constant decrease in CH₄ conversions after ca. 100 minutes TOS, indicating a faster rate of catalyst deactivation. The increase in CH₄/CO₂ ratio did not affect CO₂ conversions at 550°C, but a small increase in CO₂ conversion was registered at 750°C. It may be explained by the disproportionation reaction, in accordance with the La Chatelier's principle. At both temperatures an evident rise in H₂ formation was observed, which clearly points to the development of direct methane decomposition reaction with the increase in CH₄/CO₂ feed ratio.

The excess of CO₂ in the feed gas had no effect on CO₂ conversion at 550°C, while at 750°C it resulted in the rise of carbon dioxide conversion. At the same time, the product distribution revealed an excess of CO in comparison to the tests with equimolar CH_4/CO_2 feed ratios, suggesting that the excess of CO₂ promotes RWGS reaction, especially at 750°C. The increase in $CH_4/CO_2/Ar$ ratio from 1/1/8 to 1.5/1.5/7, similarly as in case of sample HNi100, caused a decrease in CH_4 and CO_2 conversions and H_2/CO ratios in catalytic tests carried out both at 550 and 750°C. This indicates that with the increased concentrations of both CH_4 and CO_2 , there is most probably not enough active centres able to convert substrates into CO and H_2 .

In general, the feed ratio of $CH_4/CO_2/Ar$ had a significant influence on the catalysts activity towards CO_2 and CH_4 . The excess of methane in the feed ratio enhanced decomposition of methane and thus, the formation of carbon deposits. On the other hand, the excess of CO_2 caused the decrease in H_2/CO molar ratios. Moreover, the performed catalytic tests revealed different selectivities of tested HNi100 and HNi25 samples towards DRM.



Fig. 9.19 The results of catalytic tests carried out over HNi25 catalyst in DRM reaction at 550°C for different compositions of feed gas: (A) CH_4 conversion, (B) CO_2 conversion, (C) H_2/CO molar ratio; total flow 100cm³/min, GHSV=20000h⁻¹



Fig. 9.20 The results of catalytic tests carried out over HNi25 catalyst in DRM reaction at 750°C for different compositions of feed gas: (A) CH_4 conversion, (B) CO_2 conversion, (C) H_2/CO molar ratio; total flow 100cm³/min, GHSV=20000h⁻¹

9.2.6 Stability tests

The catalyst HNi25 was selected for 24h stability tests at 550, 650 and 750°C (Fig. 9.21). At 550°C the catalyst showed unstable performance. Methane conversion increased during the first 6h TOS followed by a short-time stabilization, and further decreased after ca. 16h TOS. As already commented before, the increase in CH₄ conversion may be assigned to the occurrence of direct methane decomposition resulting in the formation of carbon deposits that finally end up passivating the catalyst surface. Moreover, the formed carbon nanotubes lifted nickel crystallites from the support, decreasing in this way the interaction between active phase and support and promoting sintering of Ni particles, as well as CH₄ decomposition. The CO₂ conversions became stable after ca. 2.5h TOS.



Fig. 9.21 The results of stability tests carried out over HNi25 catalyst for 24h at 550, 650 and 750°C: (A) CH₄ and CO₂ conversions, (B) H₂/CO molar ratios; CH₄/CO₂/Ar=1/1/8; total flow 100cm³/min; GHSV=20000h⁻¹

As temperature increased, the DRM reaction gained importance over direct methane decomposition and other side reactions, i.e. it became thermodynamically favoured. At 750°C both methane and CO_2 conversions remained completely stable over 24h tests, reaching high values

around 89 and 92%, respectively. The values of H_2/CO ratio registered at 750°C were constant and slightly below expected value of 1, i.e. equimolar H_2/CO mixture resulting from DRM.

9.3 Conclusions

Hydrotalcite-based catalysts containing nickel in brucite-like layers for dry reforming of methane were prepared using wide range of Ni loadings, for a fixed M^{2+}/M^{3+} molar ratio equal to 3. The influence of Ni-content on the physico-chemical features of this series of catalysts was analysed by means of different characterization techniques. Their activity in DRM and direct methane decomposition was tested at relatively low temperatures between 550 and 750°C.

Upon calcination of hydrotalcites, Ni was found to form a mixed oxide solid solution, together with Mg and Al, forming in this way the periclase-like structure of MgO. Reduction under $5\%H_2/Ar$ at 900°C caused the segregation of the separated Ni-phase, resulting in the formation of isolated Ni/NiO_x particles. The size of these particles increased with the increasing Ni-content. Catalysts basicity was substantially modified as a consequence of the reduction pre-treatment and depended strongly on the Ni content. The highest content of basic sites was registered for the catalyst which was synthesized by substitution of 25% magnesium cations by Ni²⁺, which resulted in Ni loading close to 20wt.%. This catalyst showed also the highest content of strong basic sites associated with O^{2-} anions.

Both the DRM and the direct methane decomposition experiments evidenced increasing methane conversion with the increasing Ni content, as a consequence of increasing Ni particle size, pointing that catalyst activity towards CH₄ was dependent mainly on Ni particle size. The CO₂ conversions measured during DRM runs at 550°C did not depend that strongly on Ni-content. They were found to approximately meet the values predicted by thermodynamics at tests carried out at 650 and 750°C. The highest conversion of CO₂ was registered for the catalyst which exhibited the highest basicity. The product distribution, i.e. H₂/CO molar ratios, obtained at 550°C was higher than the stoichiometric expected value of 1, especially for the samples with high nickel loading, but always lower than the thermodynamic limit, equal at 550°C to approximately 3.5. The physicochemical characterization of the catalysts after reaction further confirmed these facts and showed increasing carbon deposition with the increase in Ni loading. The activity of Ni-containing hydrotalcite-derived catalysts with nickel in the brucite-like layers towards CH₄ decomposition, the key-carbon-forming reaction, may be controlled through the reduction of Ni content, which results in smaller Ni particles. However, the Ni content in brucite-like layers influenced significantly also the basicity of the obtained catalysts, and thus CO₂ conversions. Therefore, based on the obtained results of the materials characterization and catalytic tests, it may be stated that the optimal content of nickel for the hydrotalcite-derived catalyst with nickel introduced into brucite-like layers should be equal or similar to this shown by sample HNi25, i.e. around 20wt.%, as this catalyst proved to be efficient during 24h stability tests carried out at relatively low temperatures 650 and 750°C.

10 Influence of promoters (Ce, Zr)

The Ni/Mg/Al hydrotalcite derived materials have been thoroughly studied in DRM reaction, as reported in previous two Chapters. In this section the work was focused on investigating the effect of ceria and/or zirconia promotion on the catalytic activity of HTs-based catalysts in dry reforming of methane.

It has been reported elsewhere [152, 233-235, 237, 238], that catalytic activity and thermal stability of Ni-based catalysts may be improved by adding promoters, such as CeO₂ and/or ZrO₂ (Chapter 4.1.2.2 and Chapter 5.5.2). The addition of Ce-species into the catalytic hydrotalcite-based structure was found to improve the reducibility of the nickel species and resulted in the introduction of new basic sites, which increases the CO₂ adsorption capacity of the catalysts. Moreover, ZrO₂ may increase the content in oxygen vacancies on the catalyst surface, which are of key importance for the dissociative adsorption of CO₂. Additionally, zirconia is known to improve materials thermal stability [159, 265].

As already mentioned in Chapter 5.5.2, the effect of ceria promotion on the catalytic activity of Ni-containing hydrotalcite-based materials in DRM has already been studied by Daza et al [114, 233-237], who introduced nickel into the hydrotalcite catalytic system either at coprecipitation stage, via reconstruction method or self-combustion method. Therefore, in this study the adsorption technique, which was already proven to be suitable for the introduction of small amounts of Ni species in case of sample HNi-AD (Chapter 8), was applied to promote HNi25 and HNi100 catalysts with ceria. These two samples were chosen because of their highest registered conversions of CO₂ and CH₄ (Chapter 9). Moreover, sample HNi25 showed the highest basicity, and exhibited much more stable performance in DRM reaction at 550°C than HNi100 catalyst, as confirmed by the characterization of the spent catalyst.

To the best of my knowledge, the zirconia promoted nickel-containing hydrotalcitederived materials have not yet been reported as a catalysts for DRM reaction. Thus the effect of zirconia promotion has also been investigated in this study. As reported by Tichit et al. [191], although Zr⁴⁺ is a tetra-valent cation, it is possible to introduce it into brucite-like layers of hydrotalcite, due to the similar ionic radii of Zr⁴⁺ to Al³⁺. Therefore, the presented research was aiming at introducing zirconia species into brucite-like layers.

10.1 Physico-chemical features of the Ce, Zr and CeZr doped HT-derived catalysts

10.1.1 XRD analysis of fresh, calcined and reduced hydrotalcite-derived catalysts

The XRD patterns acquired for the fresh hydrotalcites, as well as the calcined and reduced HT-derived catalysts are depicted in Fig 10.1 A, B and C, respectively. Before calcination (Fig. 10.1 A) all materials showed the typical layered structure of hydrotalcite. The absence of any other additional crystalline phase in the diffractograms, indicates the successful incorporation of nickel and zirconium cations into the brucite like-layers. Moreover, as expected, the adsorption of [Ce(EDTA)]⁻ species resulted in the introduction of small amounts of ceria, which was well distributed on the catalyst surface and thus was not detectable by XRD. The unit cell parameters calculated for obtained hydrotalcites (Table 10.1) showed that no significant increase was observed for basal spacing between hydrotalcite-layers (values of parameter c and c'), indicating that adsorption of [Ce(EDTA)]⁻ species did not result in ion-exchange, and cerium species were most probably deposited on the external surfaces of crystallites. At the same time all values of c and c'were within the range of values typical for CO_3^{2-} (7.65Å) and NO_3^{-} (8.79Å) [185]. On the other hand, a small increase in the values of parameter a of unit cell was registered for two zirconium containing samples. The parameter a of the unit cell describes the average cation-cation distances in brucitelike layers. Since Zr⁴⁺ cations have higher ionic radii than Al³⁺, Ni²⁺ and Mg²⁺, the increase in the values of α further confirms the successful incorporation of Zr^{4+} cations into hydrotalcite layers.

The XRD diffractograms registered for the calcined materials (Fig. 10.1 B), show two main reflection peaks at 43 and 64° 20, ascribed to periclase-like structure of Mg(Ni,Al)O mixed oxides formed upon thermal decomposition of hydrotalcite materials. For Ce or Zr-promoted catalysts low-intensity reflections observed at ca 28 and 37° 20 were also registered, pointing to the presence of cubic fluorite-like structure of CeO₂ (ICOD 00-023-1048) or ZrO₂ (01-081-1550), as both compounds give the highest intensity reflection at 20 equal to ca. 30°. The intensity of these reflections was the highest for sample HNi25-Ce, suggesting that the higher amount of ceria species was introduced to the sample with lower nickel content, when HNi25-Ce and HNi100-Ce were compared.



Fig. 10.1 The XRD diffractograms registered for ceria and/zirconia promoted catalysts: (A) hydrotalcites, (B) calcined materials, (C) reduced materials; ○ hydrotalcite; ■ MgO periclase-like structure of mixed oxides; ■ NiO; ● metallic nickel; ◆ CeO₂ or ZrO₂; △ MgNi₃; green line - ceria promoted catalysts; blue line - zirconia promoted catalysts; dark yellow line - Ce and Zr promoted catalysts;

The XRD diffractograms recorded for the catalysts activated in the stream of 5%H₂ in Ar at 900°C for 1h are presented in Fig. 10.1 C. The two samples with the highest content of nickel,

HNi100 and HNi100-Ce, showed the presence of reflections ascribed to metallic nickel. Similarly as for the calcined materials, small reflections arising from CeO₂ were distinguished in the XRD pattern of HNi100-Ce catalyst. The samples obtained by the promotion of HNi25 sample with ceria and/or zirconia exhibited much more complicated XRD diffractograms, pointing to the fact that the presence of different promoters had an essential influence on the phase composition of the reduced catalysts (Fig. 10.1 C).

Table 10.1 The unit cell parameters and type of anions present in the interlayer spaces of hydrotalcites promoted wit
ceria and/or zirconia (uncalcined samples)

Sample	Unit cell parameter <i>a</i> (Å)	Unit cell parameter <i>c</i> (Å)	c'=c/3 (Å)	Anions between brucite layers
HNi100	3.06	23.28	7.76	CO_3^{2-} and NO_3^{-}
HNi100-Ce	3.06	23.22	7.74	CO_3^{2-} and NO_3^{-}
HNi25	3.06	23.43	7.81	CO_3^{2-} and NO_3^{-}
HNi25-Ce	3.06	23.37	7.79	CO_3^{2-} and NO_3^{-}
HNi25-Zr	3.07	23.74	7.91	CO_3^{2-} and NO_3^{-}
HNi25-ZrCe	3.07	23.45	7.83	CO_3^{2-} and NO_3^{-}

The HNi25-Zr sample exhibited the highest intensity reflections arising from MgNi₃ alloy. The presence of this phase was also observed in XRD diffractograms of other HNi25-derived catalysts. However, Ce-promoted catalysts exhibited the lowest intensity of the reflections originating from MgNi₃ phase of all studied samples, suggesting that the presence of Zr promotes the formation of the latter, while the presence of Ce increases reducibility of nickel species, and thus inhibits the formation of MgNi₃. These statements are in good agreement with Ni crystallite sizes (estimated basing on XRD results) for HNi25, HNi25-Ce, HNi25-Zr and HNi25-ZrCe catalysts, which were equal to 6, 8, 6 and 7nm, respectively.

10.1.2 The elemental analysis of Ce and/or Zr promoted catalysts

Table 10.2 shows the composition of different Ce and/or Zr promoted hydrotalcitederived catalysts, as determined by ICP-MS and XRF analysis. Ni content between 17.3 and 19.6 wt.% was measured for all the catalysts derived from HNi25 sample. Ni/Mg ratios were in each case close to 0.3, corresponding to a ratio of M^{2+}/M^{3+} around 3, the typical value in naturally existing hydrotalcites. It is important to underline, that the values of this molar ratio presented in Table 10.2 slightly differ from the nominal values of 3 for two zirconia-containing samples. This may have arisen from the co-precipitation procedure leading to the raw hydrotalcite structure, and to a possible influence of the presence of Zr cation on pH modification, resulting in this slightly higher M^{2+}/M^{3+} molar ratios. The Ce content in HNi100-Ce, HNi25-Ce and HNi25-ZrCe catalysts was between 1.4 to 4.7wt.%, and was higher for the samples with lower loading of nickel. Zr contents of 2.5 and 2.74 wt.% were measured for samples HNi25-Zr and HNi25-ZrCe, respectively.

Sample	Ni (wt.%) ¹⁾	Mg (wt.%) ¹⁾	Al (wt.%) ¹⁾	Ce (wt.%) ¹⁾	Zr (wt.%) ¹⁾	Ni ²⁺ /Mg ²⁺ 2)	M ²⁺ /M ^{I3+} 2)	Al ³⁺ /Zr ⁴⁺ 2)
HNi100	58.66	-	8.92	-	-	-	3.02 (3.0)	-
HNi100- Ce	59.03	-	8.91	1.41	-	-	3.05 (3.0)	-
HNi25	19.57	23.85	11.76	-	-	0.34 (0.33)	3.02 (3.0)	-
HNi25- Ce	17.85	21.45	10.83	3.73	-	0.34 (0.33)	2.96 (3.0)	-
HNi25- Zr	17.33	24.04	9.66	-	2.50	0.30 (0.33)	3.33 (3.0)	13.05 (9.0)
HNi25- ZrCe	19.36	28.37	11.48	4.74	2.74	(0.28) (0.33)	3.28 (3.0)	14.16 (9.0)

Table 10.2 The results of elemental analysis obtained for ceria and/or zirconia promoted catalysts

¹⁾ determined by ICP-MS technique

²⁾ in parenthesis nominal values are given

10.1.3 FTIR experiments for Ce and/or Zr promoted hydrotalcites

The FTIR spectra of uncalcined samples (Fig. 10.2) show, similarly as for the samples without Ce or Zr species studied in Chapters 8 and 9, absorption bands common to all synthesized hydrotalcites. The range of 1000-1800cm⁻¹ is considered a main absorption region related to absorption of infrared radiation by anions present in the interlayer spaces. Typically for carbonate anions, absorption bands at 1370, 870 and 670cm⁻¹ were present [185]. A small shoulder at ca. 1376cm⁻¹ indicates that, apart from carbonate anions, the nitrate ions were also present between brucite-like layers of synthesized hydrotalcites. For the samples loaded with cerium species (HNi100-Ce, HNi25-Ce and HNi25-ZrCe) an additional absorption band present at 1600cm⁻¹, which arises from stretching vibrations of COO⁻ from EDTA [185, 233]. This indicates that cerium-EDTA complexes were not introduced into the spaces between brucite-like layers, since the FTIR and XRD confirmed the presence of carbonate and nitrate anions. However, the fact that FTIR results showed that EDTA complexes were present in the catalytic system, leads to a conclusion that most probably the [Ce(EDTA)]⁻ complexes were deposited on the external surfaces of crystallites.



Fig. 10.2 The FTIR spectra registered for Ce and/or Zr promoted hydrotalcite-derived catalysts; green line - ceria promoted catalysts; blue line - zirconia promoted catalysts; dark yellow line - Ce and Zr promoted catalysts; black line - parental materials

10.1.4 Textural properties of Ce and/or Zr promoted hydrotalcite-derived catalysts

The values of specific surface area, S_{BET} , total pore volume, V_{tot} , and mean pore size, derived from the N_2 adsorption isotherms (Fig. 10.3) for different HT-derived catalysts promoted with Ce and/or Zr are presented in Table 10.3. All values of textural parameters are typical for mesoporous hydrotalcite derived mixed-oxides [185, 186, 196]. Zr-doping resulted in HT-derived mixed oxides of higher specific surface area, i.e. S_{BET} increased from 114 to 229m²/g, due to the creation of smaller pores of mean pore diameter around 2nm (Fig. 10.3). The simultaneous presence of Ce and Zr species in HNi25-ZrCe sample resulted in the material, with surface area of S_{BET} =158m²/g, and intermediate pore sizes, i.e. 7nm.

Sample	S _{BET} (m²/g)	V _{tot} (cm³/g)	Mean pore diameter (nm)
HNi100	122	0.61	20
HNi100-Ce	123	0.54	18
HNi25	114	0.41	14
HNi25-Ce	102	0.33	13
HNi25-Zr	229	0.62	2
HNi25-ZrCe	158	0.56	7

Table 10.3 Textural properties of Ce and/or Zr promoted catalysts



Fig. 10.3 The adsorption/desorption isotherms recorded for Ce and/or Zr promoted catalysts and corresponding distribution of pores; black line - parental samples (unpromoted catalysts); green line - ceria promoted catalysts; blue line - zirconia promoted catalysts; dark yellow line - Ce and Zr promoted catalysts;

The values of textural parameters measured for the samples doped only with ceria species (HNi100-Ce and HNi25-Ce) were at a similar level as for their parental materials, indicating that ceria addition did not result in a significant blockage of pores. On the other hand, such effect was observed for the sample promoted with both Ce and Zr, so the catalyst into which the highest amount of ceria was introduced, as confirmed by XRF experiments. Moreover, it seems that when Ce was introduced into HNi25-ZrCe sample, it not only caused the blockage of narrow pores of the parental material (HNi25-Zr sample), but also introduced additional porosity, which could explain the decrease in S_{BET} and V_{tot} and increase in pore size (Fig. 10.3).

10.1.5 Reducibility of Ce and/or Zr promoted hydrotalcite derived catalysts

The H₂-TPR profiles acquired for the catalysts doped with either Ce and/or Zr species are compared to the parental materials in Fig. 10.4. The catalysts showed one asymmetric reduction peak centred between 400-800°C for the samples with high nickel loading and 600-900°C for the samples derived from HNi25. The amount of nickel has an influence on the shape and maximum reduction temperature of the reduction peaks. The shift to higher reduction temperatures occurred for the samples with lower Ni-loading. This may be explained by the formation of smaller nickel crystallites with stronger interactions between active phase and the support.



Fig. 10.4 H₂-TPR profiles of Ce and/or Zr promoted catalysts; green line - ceria promoted catalysts; blue line - zirconia promoted catalysts; dark yellow line - Ce and Zr promoted catalysts;

The position of maximum temperature of reduction (T_{max}) was dependent on the presence of the promoters. For the ceria promoted sample with the high nickel loading the T_{max} was shifted to higher temperature, indicating the decrease in catalyst reducibility after the small ceria addition. The opposite effect, was observed for HNi25-Ce and HNi25-ZrCe samples, as T_{max} was shifted from 835 to 810 and 820°C, respectively, when compared to HNi25 catalyst. These results are in good agreement with those reported in literature [233-235]. They also strongly suggest that the presence of magnesium in the sample affects the reducibility of ceria promoted Ni/Al and Ni/Mg/Al hydrotalcite-derived catalysts. The addition of zirconia, on the other hand, resulted in shift of T_{max} to higher temperatures.

The Ce and/or Zr promoted catalysts exhibited also small reduction peaks centred at ca. 250, 300, 415 and 600°C. The explanation of the reduction process is quite complicated as the processes of the reduction of NiO and ceria may be overlapping. The reduction of CeO₂ occurs in three stages: (i) the reduction of surface oxygen or oxygen capping species (250-300°C) [266], (ii) the reduction of surface lattice oxygen (450-600°C) [236] and total bulk reduction up to 900°C [233]. As ceria species were introduced in small amounts via adsorption method, they are most probably deposited over Mg(Ni,Al)O mixed oxides phase, and thus the additional reduction peaks may be explained by the reduction of Ce⁴⁺ to Ce³⁺.

10.1.6 Basicity of Ce and/or Zr promoted hydrotalcite-derived catalysts

The CO₂ desorption profiles recorded for the reduced catalysts are presented in Fig. 10.5 and the corresponding total basicity of materials and distribution of weak, medium and strong basic sites are summarized in Table 10.4. CO₂ desorption at different temperatures allowed the determination of the basicity of each catalyst (Table 10.4), which was substantially modified by the presence of the Ce and/or Zr promoters.

	W ¹⁾	M ²⁾	S ³⁾	Total
Sample	(%)	(%)	(%)	(µmol/g)
HNi100	49	45	6	37
HNi100-Ce	32	63	5	48
HNi25	31	27	43	104
HNi25-Ce	27	50	23	91
HNi25-Zr	29	60	11	50
HNi25-ZrCe	21	52	27	97

 Table 10.4 The total basicity of reduced Ce and/or Zr promoted hydrotalcite-derived catalysts and corresponding distribution of basic sites

 $^{1)}\mbox{percentage}$ of weak basic sites; desorption peak T<200°C

²⁾percentage of medium strength basic sites; desorption peak 200°C<T<300°C

³⁾percentage of strong basic sites; desorption peak T>300°C





The Ce and/or Zr promoted catalysts exhibited total basicity between 48-97 μ mol/g. The effect of the Ce addition was dependent on the nickel content in the parental material. HNi100-Ce sample exhibited higher total basicity than HNi100 catalyst. The opposite trend was shown by Ce-doped catalysts derived from HNi25 material. These results may be explained by the presence of magnesia in HNi25-Ce and HNi25-ZrCe catalysts. However, regardless of the decrease in total basicity observed for HNi25-derived catalysts, the addition of ceria resulted in the formation of higher amount of medium and strong basic sites. The presence of zirconia substantially hindered the adsorption of CO₂, especially due to the lower number of strong basic sites (low-coordinated O^{2-}).

10.1.7 SEM and TEM analysis

The SEM micrographs acquired for the calcined samples promoted with cerium species (HNi100-Ce and HNi25-Ce) are shown in Fig. 10.6. The prepared materials showed the same morphology as the unpromoted catalysts (cp. Chapter 8.1 and Chapter 9.1.7), and exhibited irregular shape particles. It is important to stress that no changes in catalysts morphology were

observed after the introduction of cerium species, suggesting a high dispersion and homogenous distribution of Ce on the catalyst surfaces. The EDX analysis performed in different zones of the materials, confirmed that Ce species were distributed uniformly on the surface (Fig. 10.6).



Fig. 10.6 SEM micrographs and results of EDX analysis performed for ceria promoted catalysts: (A) HNi100-Ce and (B) HNi25-Ce

A							
	spectrum1 of spectrum3	Spectrum	Ν	Иg	AI	Ni	Ce
		Spectrum1	4	41	26	23	10
		Spectrum2	4	41	25	28	7
		Spectrum3	4	40	22	23	14
	Or Think	Mean	4	41	24	25	10
x 1,000 15.00V 387 100 100 100 100 100 100 100 100 100 10	SDEC.2000-2 x 20,000 15.047 827 828 806 900 7.088	All results in weight 9	%				
		Spectrum	M	g	AI	Ni	Zr
	spectrum? Spectrum? Spectrum?	Spectrum1	20.	2	8.4	7.7	0.6
		Spectrum2	20.	5	8.8	7.1	0.6
		Spectrum3	18.	6	7.6	5.9	0.8
		Mean	19.	.8	8.3	6.9	0.7
X 10,000 15.0XV 882 380 160.7.3um	ина 2000 X 10,000 851 обб. 100.7.000, X 50,000 55.000 680 100.7.000,						
		Spectrum	Mg	Al	Ni	Zr	Ce
	spectrum1	Spectrum1	17.8	7.7	8.2	0.8	0.6
		Spectrum2	18.0	8.6	6.2	0.6	0.2
		Spectrum3	19.1	7.8	6.0	0.6	0.4
120 Martin 12 Martin		Mean	18.3	8.0	6.8	0.7	0.4
x 19.000 15.0XV 582 100 2000. 100 1.1000	x 100,000 15.0k7 COMPO 8001 100 7.1mm	All results in weight %					

Fig. 10.7 SEM micrographs and EDX analysis acquired for reduced Ce and/or Zr promoted catalysts: (A) HNi25-Ce, (B) HNi25-Zr and (C) HNi25-ZrCe



Fig. 10.8 TEM micrographs and corresponding distribution of Ni particle size acquired for Ce and/or Zr promoted catalysts: (A) HNi25-ZrCe, (B) HNi25-Zr, (C) HNi25-Ce, (D) HNi25, (E) HNi100-Ce and (F) HNi100

The reduced Ce and/or Zr promoted catalysts derived from sample HNi25 were also analysed by SEM technique (Fig.10.7). Again, similarly as for unpromoted catalysts (cp. Chapter 8.2 and Chapter 9.1.7), the structural changes of the materials were observed upon reduction in 5%H₂ in Ar at 900°C for 1h. The surface of the particles of the reduced catalysts were covered in a cauliflower-like shape aggregates. Very small aggregates were present on the surface of the Zr promoted catalysts, clearly visible in SEM images acquired for the reduced HNi25-ZrCe catalyst. The EDX analysis of different zones of materials evidenced the uniform composition of the prepared catalysts.

The TEM analysis of registered images proved that the application of Ce and/or Zr promoters influenced the Ni particle size (Fig. 10.8). The size of Ni particles was also dependent on the Ni content. The distribution of Ni particles for Ce promoted catalysts derived from HNi25 sample (HNi25-Ce and HNi25-ZrCe), were wider and mean particle sizes were larger than those recorded for their parental material. On the other hand, the HNi100-Ce sample showed lower values of Ni particle size than HNi100 catalyst. This indicates that ceria addition promotes reducibility of Ni species to an extent depending on the presence of magnesia, as well as Ni content, which is in good agreement with the results of H₂-TPR experiments and the data reported in literature [114, 233-235]. The addition of Zr did not affect the distribution of nickel particle size, as shown in Fig. 10.8. The mean values of Ni crystallites measured basing on the recorded TEM images are in good agreement with those estimated based on XRD results are were equal to 19, 18, 7, 9, 7 and 8nm for HNi100, HNi100-Ce, HNi25, HNi25-Ce, HNi25-Zr and HNi25-ZrCe, respectively.

10.2 Effect of Ce-promotion

10.2.1 Activity and selectivity in DRM at 550°C

The effect of ceria promotion was evaluated for HNi100-Ce and HNi25-Ce catalysts during isothermal DRM runs at 550°C. The results of catalytic tests of ceria-promoted catalysts, in comparison to the parental materials, are presented in Fig. 10.9. The effect of the small addition of cerium species was dependent on nickel content in the catalysts and the presence of magnesia. The Ce-promoted sample derived from Ni/Al hydrotalcite-like material exhibited increased conversion of CH₄, but lower conversion of CO₂ with respect to HNi100 sample. The conversions of CH₄ higher than those of CO₂ resulted also in the excess of H₂ in the products of the reaction with respect to the parental material. On the other hand, the opposite trend was observed for Ni/Mg/Al hydrotalcite-derived material. The ceria promotion resulted in decreased conversions of CH₄ but higher conversions of CO₂ in comparison to HNi25 catalyst.



Fig. 10.9 The results of DRM runs at 550°C over Ce-promoted catalysts: (A) CH_4 conversion (%), (B) CO_2 conversion, (C) H_2/CO molar ratio; $GHSV=20000h^{-1}$; $CH_4/CO_2/Ar=1/1/8$, total flow $100cm^3/min$

In case of both catalysts the decrease in CO_2 conversion was observed during the first 100 minutes of reaction, which may account, to a certain extent, for catalysts deactivation and loss of selectivity towards DRM. However, the positive effect of ceria promotion on stability of catalysts may be clearly observed, as CO_2 conversions for both HNi25-Ce and HNi100-Ce catalysts stabilized

within shorter period of time, and in case of the former, also reached higher values than for the unpromoted samples. According to Daza et al. [236], the promoting effect of ceria is due to the Mg and Ce synergetic effect on CO₂ adsorption capacity. As confirmed by CO₂-TPD experiments, the HNi100-Ce catalyst exhibited one of the lowest total basicities (cp. Chapter 10.6.1), which was caused, among others, by the absence of magnesia in the catalyst structure. Therefore, the different effect of ceria promotion for HNi100-Ce catalyst may be explained by the lack of synergetic effect between Ce and Mg, which enhances materials basicity.

For all tested catalysts H_2/CO ratios increased with TOS. In case of HNi25-Ce sample the H_2/CO ratio were the closest to unity from all tested catalysts, suggesting, that in this case, ceria addition shifted the selectivity of the process towards DRM. The increased basicity resulting in the increasing CO_2 adsorption capacity, together with the interaction of ceria with the carbon deposits and their gasification by the reverse Boudouard reaction, may have been the main reasons for the observed improvement in catalytic performance.

In order to understand the effect of ceria addition to Ni/Al and Ni/Mg/Al HT-derived catalyst in more detail, additional tests of direct methane decomposition were performed (Fig. 10.10). In both cases, the CH₄ conversions were lower with respect to the parental materials, indicating that ceria addition inhibits methane decomposition and the following coke formation. This effect was more evident for HNi25-Ce catalyst, as the constant decrease in CH₄ conversion was observed after around 80 minutes TOS. In case of HNi100-Ce catalysts, although Ce promotion also caused the loss of activity towards CH₄ decomposition, the CH₄ conversions were increasing with TOS, suggesting sintering of Ni particles, and thus promotion of CH₄ decomposition with TOS.



Fig. 10.10 The results of CH₄ decomposition carried out over Ce-promoted HT-derived catalysts; Temperature 550°C; GHSV=20000h⁻¹; CH₄/Ar=2/8; total flow 100cm³/min



10.2.2 The influence of the temperature



The Ce-promoted samples were tested also in DRM reaction during isothermal 5h tests at 650 and 750°C. The comparison of the catalysts performance, given as average CH_4 , CO_2 conversions and H_2/CO molar ratio as a function of temperature, is presented in Fig. 10.11. The effect of ceria

addition was the same for 650 and 750°C. It resulted in decreased conversions of CH₄ and an increase in CO₂ conversions with respect to the unpromoted catalysts. Moreover, at 750°C the product distribution, i.e. the values of H₂/CO molar ratio, were the same for Ce-promoted and unpromoted catalysts. The effect of ceria promotion was more evident for sample HNi25-Ce, which was loaded with higher ceria content than HNi100-Ce sample. The H₂/CO molar ratio decreased with comparison to the parental material and the differences between unpromoted and promoted catalysts were decreasing with the increase in temperature. Over the tested temperature range CH₄ conversions were higher than CO₂ conversions for Ni/Al derived catalyst, as well as for HNi25 sample at 550 and 650°C. Only for the HNi25-Ce catalyst the registered values of CO₂ conversion were higher than those of CH₄ at all three tested temperatures, suggesting that Ce addition to HNi25 sample resulted in the promotion of RWGS reaction, influencing in this way the distribution of the obtained products.

10.2.3 Characterization of the spent catalysts

The results of TG experiments performed for the catalysts after 5h isothermal DRM runs at 550°C are depicted in Fig. 10.12. The obtained results revealed that although ceria promotion resulted in decreased activity towards carbon forming reaction – methane decomposition (Fig. 10.10) – the Ce-promoted samples, exhibited higher mass loss than the unpromoted catalysts. These results indicate that Ce addition promoted other side reactions resulting in the formation of carbonaceous deposits. It was most probably CO₂ reduction with H₂, resulting in C and water. This could also explain the increase in CO₂ conversion observed for HNi25-Ce catalyst (Fig. 10.9). On the other hand, the decrease in CO₂ conversion and higher deposition of coke observed for HNi100-Ce sample, with respect to HNi100 catalyst may be explained by disproportionation of CO.



Fig. 10.12 The results of TG experiments performed for Ce-promoted catalysts after DRM tests carried out at 550°C

It is worth mentioning, that the addition of ceria for both catalysts led to a shift of DTG peaks to lower temperatures, indicating that ceria promoted oxidation of carbon deposits. The DTG peaks observed for all catalysts were centred at temperatures between 550-650°C, suggesting the formation of graphitic carbon during DRM reaction at 550°C. These results were confirmed by XRD measurements acquired for the spent catalysts after isothermal DRM tests at 550, 650 and 750°C (Fig. 10.14). All samples after the tests at 550°C exhibited a reflection at 2 θ equal to 26° characteristic for graphitic carbon (ICOD 03-065-6212). It was present for samples HNi100 and HNi100-Ce also after the tests at 650 and 750°C and its intensity was decreasing with the increase in temperature, pointing to the decrease in the C formation. The intensity of the reflection arising from graphitic carbon was also decreasing with the increase in temperature for HNi25 and HNi25-Ce catalysts and no graphitic carbon was registered after the tests at 750°C. Moreover, the Cepromoted catalyst showed lower intensity of this reflection than HNi25 sample, indicating that ceria addition resulted either in the inhibition of the formation of graphitic carbon or its faster removal in situ due to a side reaction (reverse Boudouard reaction). This type of carbon is considered to be inactive in DRM and hard to oxidize. Therefore, although Ce-promotion resulted in the formation of higher amounts of coke deposits, it also influenced the type of carbonaceous species formed on the catalyst surface, and, as a final result, had a positive effect on the catalyst performance. Interestingly, the HNi25-Ce catalyst after the tests at 750°C showed the presence of reflections characteristic for the hydrotalcite structure, pointing to the occurrence of 'memory effect', which suggests that RWGS reaction was well developed over the catalyst tested at 750°C.

Sample	Ni partic reduced ca	Ni particle size for reduced catalysts (nm)		le size for ited at 550°C m)	Ni particle size for catalyst	Ni particle size for catalyst	
p	XRD ¹⁾ analysis	TEM analysis	XRD ¹⁾ analysis	TEM analysis	tested at 650°C ¹⁾ (nm)	tested at 750°C ¹⁾ (nm)	
HNi100	20	19	18	21	14	15	
HNi100-Ce	19	18	19	na	11	12	
HNi25	6	7	11	13	9	8	
HNi25-Ce	8	9	8	11	7	7	

Table 10.5 The Ni particle size estimated for the reduced catalysts and the spent samples after DRM runs at 550, 650 and 750°C

¹⁾values estimated by Scherrer equation (XRD analysis)

na – no analysis

The nickel particle sizes of the reduced and spent catalysts were estimated using Scherrer equation and are presented in Table 10.5, together with the values calculated basing on TEM images of the reduced catalysts and the spent samples after the tests at 550°C. The HNi100 and

HNi100-Ce catalysts did not show considerable differences in Ni particle size after tests at 550°C. For HNi25 and HNi25-Ce catalysts the increase of Ni particle size was observed, suggesting the sintering of Ni particles. On the other hand, the values calculated for the spent catalysts after the tests carried out at 650 and 750°C, suggest that the ceria addition most probably prevents Ni species from sintering, since Ni crystallite size was smaller for Ce promoted samples with respect to HNi25 and HNi100 catalysts.





10.2.4 On the effect of the feed gas composition

The two Ce-promoted catalysts were also tested in DRM at 550°C with different compositions of feed gas, i.e. excess of CH₄, excess of CO₂ and higher concentration of CH₄ and CO₂ in comparison to the tests carried out for CH₄/CO₂/Ar ratio of 1/1/8 (Fig. 10.14 and 10.15).


Fig. 10.14 The results of catalytic tests carried out over HNi100-Ce catalyst in DRM reaction at 550°C for different compositions of feed gas: (A) CH_4 conversion, (B) CO_2 conversion, (C) H_2/CO molar ratio; total flow 100cm³/min, GHSV=20000h⁻¹

The results of the tests carried out for HNi100-Ce catalyst (Fig. 10.14) showed that excess of CH_4 in the feed gas had a positive effect on CO_2 conversion, negative effect on CH_4 conversion and led to higher formation of H_2 with respect to the tests carried out with equimolar feed gas composition, which is in good agreement with thermodynamics (cp. Chapter 7.1). On the other hand, the tests carried out in the excess of CO_2 caused a decrease in both CH_4 and CO_2 conversions. The distribution of the obtained products was also strongly affected by the feed gas composition and decreased with TOS for DRM runs carried out in the excess of CO_2 and increased with TOS for tests performed in the excess of CH_4 .



Fig. 10.15 The results of catalytic tests carried out over HNi25-Ce catalyst in DRM reaction at 550°C for different compositions of feed gas: (A) CH₄ conversion, (B) CO₂ conversion, (C) H₂/CO molar ratio; total flow 100cm³/min, GHSV=20000h⁻¹

Similar tests carried out for HNi100 sample (cp. Chapter 9.2.5) revealed that the excess of CO_2 in the feed gas led to the promotion of CH_4 decomposition and thus increased CH_4 conversions. The Ce addition clearly inhibited CH_4 decomposition and thus increased the selectivity of the process towards DRM, which is reflected in the registered values of H_2/CO close to unity for the tests carried out in the excess of CO_2 .

The results of the tests performed for HNi25-Ce catalyst are depicted in Fig. 10.15. As in the case of HNi100-Ce, the excess of CH₄ in the feed also had a negative effect on CH₄ conversion. It, however, barely affected CO₂ conversions, which after around 100 minutes TOS were at a similar level as for the tests carried out with the equimolar feed gas composition of CH₄/CO₂/Ar=1/1/8. Similarly as for HNi100-Ce sample, the presence of the excess of CO₂ caused a decrease of both CO₂ and CH₄ conversions and lowered also the values of H₂/CO. It is important to mention, that the HNi25-Ce catalyst showed the most stable performance when the excess of CO₂ was introduced to the reactor. According to thermodynamics (cp. Chapter 7.1), the application of the excess of CO₂ should have a positive effect on catalyst stability, as lower formation of carbon deposits should be expected. Additionally, Ce-promotion may help to oxidize deposited coke via reverse Boudouard reaction. These two facts may explain the most stable performance of HNi25-Ce catalyst in the tests carried out with the feed gas composition of CH₄/CO₂/Ar=1/1.5/7.5.

The change from feed gas composition $CH_4/CO_2/Ar$ of 1/1/8 to 1.5/1.5/7 led to the decrease in CH_4 , CO_2 conversions and H_2/CO ratios for all samples. For sample HNi100-Ce, the CH_4 and CO_2 conversions and product distribution followed the same trends as in the tests carried out with $CH_4/CO_2/Ar$ ratios of 1/1/8. Thus, the increasing concentration of methane and CO_2 in the feed gas had a negative effect on the performance of HNi100-Ce catalyst. On the other hand, the test performed for HNi25-Ce sample showed that the increase in the concentrations of CO_2 and CH_4 in the feed resulted in a more stable work of the catalyst, as no changes in CH_4 , CO_2 conversions and H_2/CO ratios were observed during 5h TOS.

10.2.5 Stability tests for 24h

Fig. 10.16 depicts 24h-tests carried out for HNi100-Ce and HNi25-Ce catalysts at 550, 650 and 750°C. Both catalysts evidenced an increase in CO_2 and CH_4 conversions with the increase in temperature, due to the endothermic nature of methane dry reforming. The observed changes in CH_4 conversions exhibited for HNi100-Ce catalyst at all three tested temperatures may be explained by the occurrence of direct CH_4 decomposition, which results in the formation of carbon deposits and thus the blockage of DRM active centres. This is in agreement with literature [263, 264], which reported that Ni/Al mixed oxides derived from hydrotalcites showed the highest activity in CH_4 decomposition in the temperature range of 600-700°C. Thus, it can explain the highest decrease in activity towards CH₄ for HNi100-Ce catalyst at 650°C.

The 24h-stability tests showed more stable performance for Ce-promoted sample derived from HNi25 catalyst than for HNi100-Ce sample. Moreover, the performance of this sample was very similar to that of the catalyst loaded with higher amount of nickel, especially at 750°C.



Fig. 10.16 The results of 24h stability tests carried out over HNi100-Ce and HNi25-Ce catalysts: (A) CH₄ conversion, (B) CO₂ conversion and (C) H₂/CO molar ratio; Temperature 550, 650 and 750°C; CH₄/CO₂/Ar=1/1/8; GHSV=20000h⁻¹; total flow 100cm³/min

10.3 The comparison of Ce and Zr promoters

10.3.1 Activity and selectivity in DRM at 550°C

Fig. 10.17 presents the CH₄ and CO₂ conversions, together with the H₂/CO molar ratios, registered during DRM experiments at 550°C, in the presence of Ce and/or Zr promoted hydrotalcite-derived catalysts. Even at this low reaction temperature the catalysts were notably active towards methane dry reforming and did not exhibit any significant evidence of deactivation. Although some differences between HNi25 and HNi25-Ce catalyst were observed and discussed in Chapter 10.2, both catalysts showed a very similar performance. Both CH₄ and CO₂ conversions reached comparable values (around 40%) with slightly higher conversion of CH₄ observed for HNi25. The lower methane conversion measured for HNi25-Ce catalyst together with the values of H₂/CO close to unity, point to a positive effect of Ce promotion, which may be ascribed to the decreased rate of the direct CH₄ decomposition. The promoting effect of Ce is widely known and had been ascribed to its large oxygen storage capacity, which may be favouring the oxidation of carbon deposits formed upon DRM. It is worth mentioning that the thermodynamic analysis of the DRM reaction (cp. Chapter 7) predicts the CO₂ and CH₄ conversions around 43% and 83%, respectively, resulting in high H₂/CO ratios around 4.

When zirconium was introduced into the catalytic system, both CH_4 and CO_2 conversions were considerably lower, i.e. 25% and 30%, respectively, after 5h TOS for HNi25-ZrCe catalyst. In fact, the values of CO_2 conversion were somewhat higher than those of CH_4 , during the whole experiment for these Zr-containing catalysts, in contrast to the thermodynamically forecasted trends. This was directly reflected in the obtained values of H_2/CO ratios measured during the DRM runs, which were considerably lower for Zr-promoted catalysts than for HNi25 and HNi25-Ce. As a result, zirconia addition modified the selectivity of the catalysts resulting in an excess of CO in the syngas mixture. The results of the catalytic tests with CH_4/Ar mixture in the feed (Fig. 10.18) revealed that the Zr addition drastically changed catalyst activity towards methane decomposition. It was even more evident for the catalyst doubly promoted with ceria and zirconia. In this case methane decomposition reaction was substantially inhibited in the presence of Zr-promoted catalysts, as no excess of H_2 was registered. At the same time, the other side reactions, such as direct or reverse Boudouard reaction may have been be significantly favoured.



Fig. 10.17 The results of catalytic tests performed for Ce and/or Zr promoted catalysts at 550°C; GHSV=20000h⁻¹; CH₄/CO₂/Ar=1/1/8; total flow 100cm³/min



Fig. 10.18 CH₄ decomposition over Ce and/or Zr promoted hydrotalcite-derived catalysts; CH₄/Ar=2/8; GHSV=2000h⁻¹, total flow 100cm³/min

10.3.2 The influence of the reaction temperature

The average values of CH₄ and CO₂ conversions and H₂/CO molar ratio registered during 5h isothermal tests carried out over different Ce and/or Zr promoted catalysts at 550, 650 and 750°C are depicted in Fig. 10.19. Similarly as at 550°C, the Zr-promoted catalysts exhibited conversions of CH₄ and CO₂ lower than HNi25 and HNi25-Ce. However, the differences between Zr-promoted catalysts and other samples were decreasing with the increase in reaction temperature. At 750°C all catalysts showed similar level of CH₄ and CO₂ conversions were increasing with the increase in reaction temperature. In Fig. 2009, respectively, and H₂/CO ratios around 0.93. Both CH₄ and CO₂ conversions were increasing with the increase in reaction temperature, and the latter reached equilibrium values at 650 and 750°C.

The distribution of the obtained products (Fig. 10.19 C) clearly shows that the Zr-addition changed the catalyst selectivity towards DRM. All samples exhibited similar performance at 750°C. However, the presence of promoters affected on the obtained H_2 /CO ratios. Zr-promoted samples exhibited increasing values of H_2 /CO ratios with the increase in reaction temperature, indicating the influence of CO forming reactions, especially at low temperature. On the other hand, HNi25 and HNi25-Ce catalysts exhibited decreasing values of H_2 /CO ratio with the increase in temperature, pointing to the importance of H_2 forming reactions.



Fig. 10.19 The average values of CH₄ conversion (A), CO₂ conversion (B) and H₂/CO molar ratio (C), registered during isothermal 5h tests carried out at 550, 650 and 750°C; GHSV=20000h¹; CH₄/CO₂/Ar=1/1/8; total flow 100cm³/min

10.3.3 Characterization of the spent catalysts

The activity tests towards DRM process (Fig. 10.17-10.19) proved that the competitive side reactions, such as CH₄ decomposition or Boudouard reaction, may influence the overall process to a certain extent in the presence of the different Ce and/or Zr promoted hydrotalcite-derived catalysts. The study and quantification of the carbon deposits formed upon reaction was helpful in

determining the role of the Ce and/or Zr promotion in hydrotalcite-derived catalytic systems. Transition electron microscopy (TEM) images registered after 5h DRM reaction at 550°C are presented in Fig. 10.20, together with the corresponding distribution of Ni particle size. The spent HNi25 and HNi25-Ce catalysts contained a large amount of carbon deposits. The original particles of both catalysts seem to be completely covered by these carbon formations. Ni particles are still visible, detached from the HT-derived mixed oxides structure, at the end of well-developed fishbone/whisker carbon nanofibers. These fibres contained several graphite planes, with the thickness varying from 5 to 20nm. In case of HNi25-Ce catalyst, the fibre structures contain more defects and frequently appear broken or damaged, although they still cover a significant part of the active surface.



Fig. 10.20 The TEM images acquired for: (A) HNi25-ZrCe, (B) HNi25-Zr, (C) HNi25-Ce and (D) HNi25 catalysts after 5h DRM at 550°C together with the corresponding distributions of Ni particle size.

On the other hand, such fibre structures are completely absent on the spent Zr-containing catalysts. Carbon formations resembling multi and even single wall carbon nanotubes are present on the surface and growing out of the catalysts surface. These carbon filaments are composed of only 1 to 4 graphite planar layers and sometimes form bamboo-like structures. It is important to stress, that the thickness of such structures is much lower than in case of fishbone/whisker fibres present on the surfaces of HNi25 and HNi25-Ce catalysts. For HNi25-ZrCe catalyst some fishbone structures were found, but in insignificant amount as compared to HNi25 and HNi25-Ce catalysts. Thus it may be concluded that the presence of Zr had a significant influence on the type of carbon deposits formed on the catalysts surface. The TEM images confirmed that Zr addition substantially inhibited the formation of carbon deposits in the direct methane decomposition.

Fig. 10.21 presents the results of thermogravimetric measurements registered for the spent Ce and/or Zr promoted catalysts after 5h DRM reaction at 550°C.



Fig. 10.21 The thermogravimetric oxidation of carbon deposits in the spent Ce and/or Zr promoted HT-derived catalysts: (A) mass loss and (B) derivative of mass loss as a function of temperature

It can be clearly observed, that for HNi25 and HNi25-Ce catalysts higher amounts of carbon deposits were formed during 5h DRM reaction at 550°C. As confirmed by TEM images, both catalysts exhibited fishbone-like fibres on the surface. These carbon deposits were oxidized at lower temperatures in the presence of Ce, and the difference between T_{max} of the peaks registered for both catalysts (Fig. 10.21) was equal to ca. 25°C.

The thermogravimetric curves registered for Zr-promoted catalysts were completely different from those for the other samples. A wide DTGA peak starting at around 300°C and extending up to maximally 525°C was observed for both HNi25-Zr and HNi25-ZrCe. The area of these peaks was much smaller in comparison to HNi25 and HNi25-Ce, indicating that the carbon formation during DRM was minimal or substantially reduced, when Zr was present in the HT-derived catalytic system. The lowest mass loss was exhibited by the sample promoted with both Ce

and Zr with respect to other catalysts, proving the beneficial effect of the addition of these two elements.

The XRD patterns registered for the promoted catalysts after 5h DRM runs at 550°C are compared in Fig. 10.22. The obtained results are in a good agreement with the TEM and TG experiments. The Zr-promoted catalysts showed no reflection arising from graphitic carbon (2θ around 26°), in contrast to HNi25 and HNi25-Ce catalysts. When Ce was added to the catalyst, however, the reflection from graphitic carbon was of much lower intensity than for HNi25. Moreover, Zr-promoted samples showed much lower intensity of reflections arising from the metallic nickel structure (2θ around 44, 51 and 76°). These results are in good agreement with the values measured basing on TEM images (Fig. 10.20). The Zr addition resulted in the formation of small nickel crystallites around 4nm, which led to the inhibition of carbon forming reactions and thus, to the increased catalysts stability. It may be concluded, that the Zr promotion modified the selectivity of DRM catalysts by activating the DRM route and, to some extent, the Boudouard reaction with a simultaneous almost complete inhibition of direct methane decomposition. Therefore, the application of Zr as a promoter in the HT-derived catalysts seems to guarantee high catalyst stability.



Fig. 10.22 The XRD diffractograms registered for spent Ce and/or Zr promoted catalysts after 5h TOS DRM catalytic tests at 550°C; ●metallic nickel, ■ periclase-like mixed oxides, △ MgNi₃, ▼ graphitic carbon

The explanation of such high resistance to coke formation in case of Zr-promoted samples may be explained on the basis of physico-chemical characterization of these materials. As confirmed by low temperature N₂ sorption experiments (Fig. 10.3, Table 10.3), HNi25-Zr catalyst exhibited the narrowest distribution of pores and the highest specific surface area in comparison to other Ce and/or Zr promoted catalysts. This increase in the value of S_{BET} and the favoured presence of narrower pores may explain a higher resistance towards deactivation due to a limited growth of carbon fibers. However, this does not explain lower activity of Zr-containing samples. The XRD and TEM experiments proved that the presence of Zr had a positive effect on the Ni particle size, and resulted in the formation of smaller crystallites of Ni in comparison to other catalysts. Taking into account, that, as reported in literature, large Ni crystallites promote direct methane decomposition, it may explain lower activity towards methane of Zr-containing samples. Moreover, CO₂ adsorption is enhanced on small metal particles [246], which would favour reverse Boudouard reaction, resulting in an increased CO formation. This is in good agreement with the low values of H₂/CO molar ratio registered for Zr-promoted catalysts (Fig. 10.19 C). Moreover, the H₂-TPR experiments confirmed that Ce addition to HNi25 catalyst resulted in the increase of catalyst reducibility, while Zr addition had an opposite effect, in complete agreement with TEM and XRD observation. The CO₂-TPD experiments showed that Zr promotion hinders the adsorption of CO₂ on the strong basic sites, while Ce addition seemed to favour strong basicity. The obtained results revealed that the presence of Zr affected CO₂ adsorption pattern that, in turn, modified the reaction pathway.

10.3.4 Stability tests for 24h

The sample HNi25-ZrCe, which showed the lowest amount of carbon deposits after 5h DRM catalytic tests at 550°C was chosen for 24h stability tests carried out at 550, 650 and 750°C. The results of these tests are depicted in Fig. 10.23. At all three tested temperatures the CO₂ conversions were higher than those of CH₄, which resulted in the excess of CO in the products of the reaction and suggests the occurrence of RWGS reaction. The difference between CO₂ and CH₄ conversions were the highest at 650°C and for this temperature the lowest values of H₂/CO ratios were registered. The catalyst showed constant slow decrease in conversions of both CO₂ and CH₄ at tested temperatures, indicating the deactivation of catalyst with TOS. This effect was decreasing with the increase in temperature and may have been caused by the formation of carbon deposits which blocked narrow pores of the catalyst.

The characterization of the catalysts studied in this Chapter revealed that the lowest amount of carbon deposits was formed over HNi25-ZrCe catalyst. However, as the material showed slow deactivation with TOS, further tests and research should be carried out in order to improve the stability of Zr and Ce promoted catalysts, including the evaluation of the influence of the molar Ce/Zr ratio on the catalytic behaviour.



Fig. 10.23 The results of 24h stability tests over HNi25-ZrCe catalyst carried out at 550, 650 and 750°C; GHSV=20000h⁻¹; CH₄/CO₂/Ar=1/1/8; total flow 100cm³/min

10.4 Conclusions

The Ni/Mg/Al and Ni/Al hydrotalcite-derived materials were synthesized in the presence of either Ce and/or Zr and applied as catalysts for syngas production through dry reforming of methane at 550, 650 and 750°C. The characterization of the materials showed that Ce species were present as a separate phase on the materials surface, while Zr⁴⁺ cations were successfully incorporated into the brucite-like layers of catalysts precursors. The presence of the promoters was found to strongly determine both the activity and the selectivity of these catalysts. The addition of Ce-species into the catalytic hydrotalcite-based structure resulted in an increased reducibility of the nickel species for HNi25 derived catalyst, and in the introduction of new strong (O²⁻) and intermediate strength (Lewis acid-basic pairs) basic sites, which increased the CO₂ adsorption capacity of the prepared materials. The characterization of the spent catalysts showed that Ce addition led to the formation of higher amount of carbon deposits with respect to the unpromoted samples. However, the type of carbon deposits changed, and lower amounts of undesired graphitic carbon were observed over Ce-promoted samples in comparison to unpromoted catalyst. Moreover, Ce-promoted samples showed lower activity towards CH₄ decomposition.

Zirconia addition considerably inhibited the direct methane decomposition reaction, favouring the interaction of methane with CO₂ together with other important parallel reactions, such as reverse Boudouard reaction. Though lower conversions of both methane and CO₂ were measured for Zr-containing samples, almost no carbon was deposited on the catalysts surface upon 5h of DRM reaction at 550°C. Carbon nanotubes were formed upon direct methane decomposition on Ni-containing catalysts.

The physicochemical characterization of the catalysts showed the formation of narrower porosity, resulting in higher surface areas for HNi25-Zr and HNi25-ZrCe catalysts. The XRD and TEM measurements confirmed the formation of small Ni crystallites (around 4nm) in these two catalysts, which were considerably smaller than for HNi25 and HNi25-Ce (around 12nm). These small Ni crystallites were not active in direct methane decomposition and favoured other side reactions, i.e. reverse Boudouard reaction. Moreover, the presence of Zr was found to promote the adsorption of CO₂ on weak and moderate strength basic sites, resulting in the favoured interaction of adsorbed CO₂ with methane, and thus enhancing selectivity towards DRM.

11 Conclusions

The presented PhD Thesis was focused on the application of hydrotalcite-derived catalysts for dry reforming of methane, which is one of the methods of chemical CO₂ utilization. The analysis of literature concerning the means of valorisation of carbon dioxide presented in Chapter 3, proved that DRM may become an important industrial process to produce synthesis gas. It is an alternative to steam reforming or partial methane oxidation processes. Another important future application of DRM will be in Chemical Energy Transmission and/or Storage systems (CETS). The commercialization of the process is, however, limited until a low-cost, active and stable catalyst is offered to industry.

A number of different materials have been tested as catalysts for DRM reaction. Current research is focused on Ni-based materials supported on single oxides (Al₂O₃, MgO, SiO₂, CeO₂, TiO₂, ZrO₂), mixed oxides (MgO-Al₂O₃, CeO₂-ZrO₂), natural clays, zeolites or carbon materials (activated carbon, carbon nanotubes), as presented in Chapter 4. Some of these materials positively affect the catalyst performance, such as e.g. increased interactions between nickel active phase and support resulting in the inhibition of sintering of Ni species and thus in the increase in the resistance to coke formation. Mixed alumina-magnesia has been reported to show these beneficial effects.

The application of hydrotalcite-derived materials in DRM has been proven to give materials with desired properties in DRM reaction, such as high basicity, relatively high specific surface area and homogenous distribution of nickel species, as presented in Chapter 5. Moreover, the composition of HTs may be tailored at the synthesis stage or via various modifications of such materials, such as e.g. ion-exchange or reconstruction method. However, despite some literature reports, several aspects of hydrotalcite applications in DRM have not yet been solved. Therefore, the presented studies focused on the preparation of Ni/Mg/Al and Ni/Al hydrotalcite-like materials into which nickel was introduced by different techniques and in different loadings. Some of the prepared materials were additionally promoted by Ce and/or Zr species.

The prepared catalysts were characterized by Inductively Coupled Plasma Mass Spectrometry ICP-MS and/or X-ray fluorescence XRF (catalysts composition), low temperature N₂ sorption experiments (evaluation of textural properties), X-Ray diffraction XRD (studies of materials structure), temperature-programmed reduction H₂-TPR (reducibility of Ni species), temperatureprogrammed desorption of CO₂ (evaluation of basicity), infrared spectroscopy (structure of catalyst precursors), transmission electron microscopy TEM and scanning electron microscopy SEM (morphology of prepared materials and thermogravimetric measurements (evaluation of catalysts stability upon DRM reaction). The characterized catalysts were evaluated in the reaction of dry methane reforming.

The research was divided into three main parts: (i) the evaluation of the effect of nickel introduction method into hydrotalcite structure, (ii) the investigation of catalytic properties of HTsderived catalysts with different nickel content introduced into HTs brucite-like layers and (iii) the effect of ceria and/or zirconia promoters on the catalytic properties in DRM.

Basing on the physico-chemical characterization of the prepared materials, the following conclusions may be drawn:

- XRD analysis of freshly prepared materials confirmed a successful synthesis of desired hydrotalcite-like materials with either CO₃²⁻ and/or NO₃,⁻ or [Ni(EDTA)]²⁻ anions in the interlayer spaces. Only for ceria promoted samples, an additional phase of CeO₂ was observed. Other elements were successfully incorporated into HTs structure.
- Elemental analysis confirmed that the desired compositions of hydrotalcite-like materials were obtained ,i.e. expected Ni²⁺/Mg²⁺, M²⁺/M³⁺, Al³⁺/Zr⁴⁺ molar ratios, and thus that the preparation of such catalysts may be strictly controlled.
- FTIR spectra of the synthesized materials exhibited absorption bands typical for hydrotalcites. Additionally, FTIR analysis confirmed the presence of different [Mⁿ⁺(EDTA)]⁽⁴⁻ⁿ⁾⁻ species in the catalytic systems modified by adsorption method.
- The evaluation of textural properties showed that all samples exhibited values of S_{BET} and V_{tot} characteristic for mesoporous hydrotalcite-derived materials. The introduction of Zr resulted in the increase of S_{BET} due to the formation of narrow pores in comparison to other materials. When nickel was introduced onto the catalyst surface as was the case for the introduction of Ni via adsorption and impregnation methods, it had no significant influence on the values of textural parameters. On the other hand, the addition of ceria caused partial blockage of pores but, in the same time, led additionally to the formation of a new type of porosity.
- The analysis of materials basicity (CO₂-TPD) showed that all catalysts had three types of basic sites: (i) weak basic sites associated with Brønsted OH⁻ groups, (ii) intermediate strength basic sites (metal-oxygen Lewis acid-base pairs) and (iii) strong basic sites (low coordinated O²⁻ anions, Lewis base). The total basicity of

the prepared materials and distribution of weak, medium and strong centres was dependent on the method of nickel introduction, nickel content and presence of promoters.

- H₂-TPR profiles recorded for the investigated catalysts showed that nickel introduced into hydrotalcite-based catalytic system exhibited strong interactions with the support and thus was reduced at temperatures above 600°C. The type and strength of the nickel interactions with the support was also dependent on the method of nickel introduction, content of magnesia and application of Ce and/or Zr promoters.
- The analysis of XRD patterns of the calcined materials showed that the applied conditions of hydrotalcite thermal decomposition were sufficient to completely destroy the layered structure and obtain Mg(Ni,Al)O, Ni(Al)O or Mg(Ni,Al,Zr)O nano mixed-oxides with periclase-like structure.
- SEM and TEM analysis confirmed the successful preparation of well crystalized hydrotalcite-derived mixed oxides with a homogenous composition. The calcined materials exhibited flake-like shaped particles. The separate phase of NiO was not observed, confirming the successful incorporation of Ni into Mg(Al)O periclaselike mixed oxides. The morphology of the samples changed upon reduction, as nickel species were extracted from the structure of mixed oxides and deposited on their surface creating in this way cauliflower-like aggregates on the support. The analysis of TEM pictures of the resulting catalysts allowed to evaluate the distribution of Ni particle size, which was strongly dependent on the method of nickel introduction, the nickel content in brucite-like layers and presence of Ce and/or Zr promoters.

The evaluation of the effect of the method of nickel introduction into hydrotalcite structure (Chapter 8) on catalytic performance in DRM process was carried out by the comparison of four HTs-derived catalysts into which nickel was introduced by: (i) co-precipitation in the solution of Na₂CO₃, (ii) impregnation method, (iii) co-precipitation in the solution of [Ni(EDTA)]²⁻ complexes and (iv) adsorption from the solution of [Ni(EDTA)]²⁻ chelates, resulting in the nickel species introduced into brucite-like layers, onto hydrotalcite surface, into interlayer spaces and onto HT surface, respectively. The samples were tested in DRM reaction in temperature-programmed and isothermal experiments carried out at 550°C. The obtained results of catalytic tests allow to draw the following conclusions:

- The catalyst with nickel introduced via impregnation method exhibited the highest CO₂ and CH₄ conversions during both temperature-programmed and isothermal tests. The high activity of this catalyst may be attributed to the presence of well dispersed nickel species on the catalyst surface. However, the sintering of Ni crystallites was observed in the catalyst after DRM runs.
- The highest activity per gram of active phase was exhibited by the sample into which nickel was introduced by adsorption method, which resulted in less than 1wt.% Ni loading. This catalyst exhibited at high temperatures (above 700°C) the performance similar to that registered for the samples loaded with ca. 7wt.% Ni. Such high activity of the catalyst was attributed to the formation of very small (non-detectable by XRD) Ni particles, well dispersed on the catalyst surface. This sample showed very high temperature of reduction of NiO (results of H₂-TPR).
- The obtained values of H₂/CO ratios were below unity for all catalysts, which suggests the occurrence of RWGS reaction. This was confirmed by XRD characterization of the spent co-precipitated sample with nickel species present in brucite-like layers, as upon DRM reaction the partial reconstruction of layered structure occurred.
- The activity of the catalysts prepared by impregnation or co-precipitation in the Ni-EDTA complexes was very similar during isothermal tests at 550°C. Both catalysts exhibited similar values of Ni particle size and total basicity, and were loaded with similar content of Ni ca. 7wt%. In comparison to other tested catalysts they exhibited also the highest concentration of strong basic sites, and this high basicity was the reason for the enhanced catalytic activity towards DRM.
- Low activity in DRM was observed for co-precipitated sample with nickel in brucite-like layers. This was caused by the low Ni content. The performance of this type of catalyst may be thus improved by increasing Ni loading.

The effect of the nickel content in brucite-like layers was studied by the preparation of catalysts in which 5, 15, 25, 50, 75 or 100% of Mg^{2+} in brucite-like layers was substituted by Ni^{2+} cations, with respect to naturally occurring hydrotalcite mineral $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$. Such substitution resulted in the materials with Ni loading between 3 and 60wt%. All prepared catalysts were tested in the isothermal tests at 550°C, and two most active catalysts were selected for additional tests at higher temperatures (650 and 750°) and with different feed gas compositions. The following conclusions may be drawn from this study:

- The activity towards methane conversion in DRM of the prepared catalysts was decreasing with the decrease in nickel content and was dependent on the Ni particle size, which followed the same trend, as observed in XRD and TEM experiments. Thus CH₄ conversions were strongly affected by the occurrence of direct CH₄ decomposition, which proceeds more easily on large Ni crystallites. The highest CH₄ conversions were registered for HNi75 sample (ca. 50wt%Ni).
- The CO₂ conversions were at a similar level for the samples with medium and high nickel content. The relation between activity towards CO₂ and catalyst basicity (especially concentration of strong basic sites) was observed. The highest conversions of CO₂ were observed for HNi25 catalyst (ca. 20wt.%Ni).
- The characterization of the catalysts after reaction showed increasing carbon deposition with the increase in Ni loading. Thus, the stability of the catalysts may be controlled through the reduction of Ni content, which results in smaller Ni particles.
- The catalytic tests for selected samples (HNi25 and HNi100) showed that equilibrium conversions of CO₂ were reached for both catalysts at 650 and 750°C.
- The tests with different feed gas compositions showed that adjusting CH₄/CO₂ ratio in the feed strongly affects catalytic performance. However, the extent to which the feed composition influenced the DRM results was dependent the nickel content and the presence of magnesia.
- Basing on the obtained results it was concluded that the optimal ratio of Ni²⁺/Mg²⁺ in hydrotalcite precursor with Ni present in brucite-like layers is equal to 1/3, as HNi25 catalyst exhibited the highest activity and stable performance during 24h stability tests carried out at 550, 650 and 750°C.

The effect of Ce and/or Zr promoters was investigated by promotion of two catalysts with Ni introduced into brucite-like layers which showed the highest catalytic performance in DRM at 550°C i.e. HNi100 and HNi25. The cerium species were introduced into hydrotalcite by adsorption from the solution of [Ce(EDTA)]⁻ chelates. Zirconium species were introduced into brucite-like layers at the co-precipitation stage. The proposed method of introduction of Ce species into hydrotalcite-like catalytic systems for DRM and effect of Zr promotion has not yet been reported in literature. The conclusions from the this part of the studies are:

- The Ce addition influenced catalysts properties, such as basicity, textural parameters, reducibility and Ni particle size. The effect of the modification of catalytic properties by cerium species was dependent on Ni content and the presence of magnesia.
- Ce promotion resulted in the formation of higher amounts of carbon deposits in comparison to the unpromoted samples. However, it also changed the type of carbonaceous deposits, as lower amounts of poisonous graphitic carbon were observed in this case. Moreover, as confirmed by XRD experiments, carbon fibers observed on the catalysts surface after reaction, were damaged and broken in comparison to the unpromoted catalyst, pointing to the beneficial effect of ceria addition which led to a partial oxidation of carbon deposits by reverse Boudouard reaction.
- The tests with CH₄/CO₂/Ar feed of 2/0/8 showed that Ce addition partly suppressed direct CH₄ decomposition over the tested, Ce promoted catalysts. This effect was even more evident for zirconia promoted catalyst.
- The addition of zirconia resulted in the formation of very small nickel particles around 4nm, which did not undergo sintering upon 5h of DRM reaction at 550°C. Such small nickel crystallites explained low activity of the catalysts towards direct CH₄ decomposition. Additionally, the small nickel crystallites favoured reverse Boudouard reaction.
- The decrease of activity towards CH₄ and CO₂ was observed for Zr-promoted catalysts in comparison to the unpromoted or only Ce-promoted samples. However, minimal formation of carbon deposits was observed for the Zr-promoted materials with respect to other samples, pointing to a very beneficial effect of Zr addition on catalysts stability.

The results presented in this PhD studies confirmed that catalytic properties of hydrotalcite-derived catalysts may be tailored by implementation of :

- (i) method of nickel introduction,
- (ii) nickel content in brucite like layers, i.e. Ni²⁺/Mg²⁺ and M²⁺/M³⁺ molar ratios, and
- (iii) the presence of Ce and/Zr promoters.

The prepared catalysts showed very good catalytic performance in DRM process. The studies on the methods of nickel introduction showed that appropriate technique may result in a

very active catalyst with very low Ni loading (below 1wt.%). The investigation on Ni content in brucite-like layers proved that the best catalytic performance was exhibited by the sample obtained by the substitution of 25% of Mg²⁺ by Ni²⁺ (Ni loading around 20wt.%). The stability and resistance towards the formation of coke deposits for this catalyst may be additionally enhanced by the promotion by Ce and Zr. Zr seems to be the guarantee for the stable hydrotalcite-derived catalyst for DRM. Further research in this area will allow to develop even more active, selective and stable catalyst for dry reforming of methane, allowing in this way a future commercialization of the process.

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Summary

The growing emissions of carbon dioxide forced implementation of different CO_2 emissions reduction strategies, which may be divided into two main groups: (i) carbon capture and storage (CCS) and (ii) carbon capture and utilization (CCU) technologies. The latter approach allows to convert CO_2 into added-value products, creating in this way a carbon cycle. It is predicted that in the near future, due to the implementation of technologies applying CO_2 as a chemical feedstock, a new carbon dioxide-based economy will be created. One of the processes that converts CO_2 into added-value products is dry reforming of methane (DRM). The process produces industrially important mixture of H₂ and CO and may be considered as an attractive route for syngas production, alternative to the currently applied steam reforming reaction. DRM possesses a number of advantages, such as: (i) it yields syngas with lower H₂/CO ratio, suitable for Fischer-Tropsch synthesis and production of oxygenated organic compounds, (ii) it supports the idea of sustainable development via recycling of CO_2 and (iii) it may be applied in Chemical Energy Transmission and/or Storage systems (CETS) for transport and storage of energy. It should be mentioned, however, that DRM process has not yet been commercialized due to the low price of CO_2 , high endothermicity of the reaction and lack of cheap, active and stable catalysts.

The literature study revealed that the most efficient catalytic systems applied for DRM process should be based on nickel as an active phase and mixed magnesia-alumina supports. The beneficial application of Ni comes from the fact that it is the most active metal in DRM reaction, which may be applied on the industrial scale. Although the noble-metal based catalysts showed higher activity in DRM, their application in large-scale DRM plants is limited due to high price and low availability. However, nickel based catalytic systems suffer deactivation upon DRM due to the formation of carbon deposits and sintering of active phase. Different strategies were proposed in literature to increase the stability of Ni-based catalytic systems. The most common ones include the application of supports and/or promoters with high basicity in order to increase CO₂ adsorption capacity, as well as to improve oxidation of carbonaceous species via reverse Boudouard reaction. Another approach is to increase interactions between nickel active phase and support and thus inhibit sintering. The application of mixed magnesia and alumina supports allows to introduce two necessary properties, as MgO possesses basic character and Ni is strongly bonded with MgO and Al₂O₃ due to the formation of NiO-MgO solid solution and/or NiAl₂O₄ spinel phase, respectively.

The materials which have beneficial properties in DRM reaction and may include desired catalysts components i.e. Ni, MgO and Al_2O_3 are hydrotalcites. The literature studies on nickel-containing hydrotalcite-derived materials for DRM have shown that such materials are very active

and stable. Therefore, the main goal of this PhD thesis was to evaluate catalytic performance of different hydrotalcite-based catalytic systems containing nickel in methane dry reforming process. Literature review showed that there are several areas of research concerning application of HTs-derived materials in DRM which has not yet been studied. The work carried for this PhD was thus aimed at filling these gaps, and was divided into three parts: (i) the comparison of the influence of nickel introduction into HTs-based catalytic system, (ii) the evaluation of wide range of nickel content in hydrotalcite brucite-like layers on materials catalytic properties and (iii) the evaluation of the effect of Ce and/or Zr promoters. In order to address these issues a number of different hydrotalcite-based catalysts was synthesized by co-precipitation method. The physico-chemical properties of the prepared materials were evaluated by means of elemental analysis (XRF or ICP-MS), XRD, FTIR, low temperature N₂ sorption, H₂-TPR, CO₂-TPD, TEM, SEM and TG experiments. The materials were subsequently tested in the DRM reaction. Most of catalytic tests were carried out at 550°C, which is considered low temperature for this process, but higher temperatures (650 and 750°C) were also studied. It should be mentioned that, the application of low reaction temperatures is beneficial from an economic standpoint.

The effect of nickel introduction method was evaluated by the comparison of catalytic performance of four hydrotalcite derived catalysts into which nickel was introduced by: (i) coprecipitation in the solution of Na₂CO₃, aimed at the introduction of nickel species into brucite-like layers, (ii) impregnation method resulting in the introduction of Ni species onto hydrotalcite surface, (iii) co-precipitation in the solution of [Ni(EDTA)]²⁻ complexes, aimed at the introduction of Ni chelates into hydrotalcite interlayer spaces and (iv) adsorption from the solution of [Ni(EDTA)]²⁻ complexes, aimed at introducing Ni species onto the HT surface. The latter technique of the catalyst preparation has not been reported in the literature concerning DRM reaction. The characterization of the prepared materials revealed that the desired hydrotalcite precursors were successfully synthesized. The nickel content in the prepared samples varied from 0.8 to ca. 8wt.%. The physicochemical properties of the catalysts were dependent on the nickel introduction method. The highest activity in DRM reaction was shown by the sample prepared by impregnation method, which exhibited CO₂ and CH₄ conversions over 90% at 750°C. This was attributed to a high dispersion of nickel species. However, the highest activity per gram of active material was exhibited by the sample into which nickel was introduced via adsorption technique, due to the formation of highly dispersed very small nickel crystallites/aggregates on the catalyst surface strongly bonded with the support.

The influence of nickel content was investigated by the preparation of catalyst precursors with nickel present in brucite-like layers. Different catalysts were synthesized by substitution of 5,

15, 25, 50, 75 or 100% of Mg²⁺ in brucite-like layers by Ni²⁺ with the respect to naturally occurring hydrotalcite mineral Mg₆Al₂(OH)₁₆CO₃·4H₂O. The characterization of the prepared materials confirmed the successful synthesis of hydrotalcite-like materials with a desired content of nickel, which varied from ca. 3 to 59wt.%. The properties of the materials, such as reducibility, basicity, Ni/NiO particle size or S_{BET}, were dependent on the nickel content. The CH₄ conversions exhibited by the prepared materials were found to be strongly influenced by the Ni particle size, and thus by the occurrence of direct methane decomposition. On the other hand, CO₂ conversions were mostly affected by the basicity of the materials, especially the concentration of strong basic sites. The best catalytic performance was shown by the sample which was obtained by the substitution of 25% of Mg²⁺ by Ni²⁺, as this catalyst showed the highest conversions of CO₂, reaching the equilibrium values at 650 and 750°C as well as high conversions of methane. Moreover, this catalyst showed a stable performance during 24h-stability tests. Therefore, it may be concluded that the optimal composition of Ni/Mg/Al hydrotalcite-derived catalyst containing nickel in brucite-like layers is around 20wt.% of Ni for the fixed M²⁺/M³⁺ ratio of 3.

The influence of Ce and/or Zr promoters was evaluated by the preparation of different HT-derived catalysts into which ceria was introduced via adsorption from the solution of [Ce(EDTA]⁻ complexes, while Zr⁴⁺ cations were introduced into brucite-like layers by a partial substitution of Al³⁺ cations. Both promoters positively influenced catalysts performance. The effect of Ce addition was dependent on the nickel content and the presence of magnesia in the catalyst. In general, Cepromotion influenced the reducibility of nickel species and thus nickel particle size, as well as the type of carbon deposits formed upon DRM reaction and thus catalyst stability. The increased stability of the material was attributed to the inhibition of direct methane decomposition and, additionally, oxidation of carbon deposits via reverse Boudouard reaction. The Zr promotion resulted in decreased activity of the catalysts. However, it strongly increased catalysts selectivity towards DRM by the inhibition of direct CH₄ decomposition. Moreover, the spent catalysts exhibited a minimal formation of coke deposits. The 24h-stability tests of doubly promoted (by Zr and Ce) catalyst showed a slight decrease in activity with TOS at 550, 650 and 750°C. This indicates that further research in this area is required in order to optimize the catalyst composition e.g. Ce/Zr molar ratio. Nevertheless, it seem that Zr promotion is a guarantee of active and stable hydrotalcite-derived catalyst for DRM.

Streszczenie pracy

Wzrastająca z roku na rok emisja ditlenku węgla wymusiła wprowadzenie nowych strategii mających na celu ograniczenie ilości CO₂ wprowadzanego do atmosfery. Zaproponowane rozwiązania można podzielić na metody sekwestracji lub utylizacji ditlenku wegla. Metody chemicznej utylizacji CO₂ pozwalają na jego konwersję do pożądanych produktów chemicznych np. paliw syntetycznych., dzięki czemu, zgodnie z przewidywaniami, w najbliższej przyszłości powstanie nowa gospodarka bazująca na ditlenku węgla. Jednym z procesów, dzięki któremu możliwa jest konwersja CO₂ do innych związków chemicznych jest proces suchego reformingu metanu. W procesie tym otrzymywany jest gaz syntezowy (mieszanina H_2 i CO), który znajduje zastosowanie w wielu technologiach przemysłu chemicznego. W porównaniu do reformingu parowego, który jest konwencjonalną metodą otrzymywania gazu syntezowego, w wyniku suchego reformingu metanu otrzymuje się równo-molową mieszaninę wodoru i CO. Jest to istotne ponieważ gaz syntezowy o takim składzie może być bezpośrednio wykorzystany np. w procesie Fischera-Tropscha do otrzymywania paliw ciekłych. Dodatkowo wprowadzenie procesu suchego reformingu metanu na skalę przemysłową, a przez to zmniejszenie emisji CO₂ do atmosfery, jest zgodne z ideą zrównoważonego rozwoju. Kolejną zaletą procesu jest możliwość wykorzystania go do transportu i magazynowania energii. Pomimo wielu zalet, proces suchego reformingu metanu nie został jeszcze wprowadzony na skalę przemysłową. Główną przyczyną ograniczonych możliwości komercjalizacji procesu suchego reformingu jest brak odpowiedniego katalizatora charakteryzującego się wysoką aktywnością i odpornością na tworzenie depozytów węglowych.

Przegląd dostępnej literatury wykazał, że najbardziej efektywne katalizatory dla procesu DRM oparte są na bazie niklu naniesionego na mieszany tlenek magnezu i glinu. Badania skupiają się na katalizatorach niklowych, ponieważ metal ten jako materiał aktywny wykazał się podobną aktywnością do metali szlachetnych, ale jest od nich dużo tańszy oraz bardziej dostępny. Katalizatory na bazie niklu ulegają jednak deaktywacji w procesie suchego reformingu metanu, co spowodowane jest (1) wysoką temperaturą prowadzenia procesu, przez co ułatwione jest spiekanie krystalitów niklu, oraz, (2) zachodzeniem reakcji ubocznych, w wyniku których powstają depozyty węglowe na powierzchni katalizatora. W literaturze zaproponowano różne strategie mające na celu zwiększenie stabilności katalizatorów na bazie niklu. Do najbardziej popularnych należy stosowanie nośników i/lub promotorów posiadających właściwości zasadowe, które zwiększają adsorpcję CO₂ na powierzchni katalizatora podczas reakcji, co ułatwia utlenianie powstałych depozytów węglowych w reakcji Boudouarda. Inną proponowaną strategią jest zwiększenie oddziaływań pomiędzy materiałem aktywnym a nośnikiem, co utrudnia spiekanie krystalitów niklu. Zastosowanie mieszanych tlenków MgO oraz Al₂O₃ pozwala na polepszenie właściwości katalizatora. MgO posiada właściwości zasadowe. Oba tlenki mogą również wykazywać silne oddziaływania z NiO, poprzez formowanie się roztworu stałego MgO-NiO we wszystkich stosunkach Ni/Mg oraz powstawanie fazy spinelowej NiAl₂O₄.

Materiałami, które posiadają korzystne właściwości w reakcji suchego reformingu metanu oraz mogą zawierać w swojej strukturze pożądane dla reakcji komponenty tj. Ni, MgO oraz Al₂O₃, są hydrotalkity. Literatura dotycząca zastosowania materiałów pochodzenia hydrotalkitowego zawierających nikiel w procesie DRM potwierdza wysoką stabilność i aktywność badanych układów. Jednakże, szereg zagadnień dotyczących aktywności katalitycznej tego typu materiałów w reakcji suchego reformingu metanu wciąż nie zostały zbadane. Przedstawiona praca doktorska koncentruje się na uzupełnieniu tych wiadomości i została podzielona na trzy główne części. W części pierwszej (Rozdział 8) przebadano wpływ metody wprowadzania niklu do układów hydrotalkitowych na ich aktywność katalityczną. Druga część (Rozdział 9) dotyczyła wpływu ilości niklu w warstwach brucytowych na stabilność, selektywność i aktywność badanych układów. W ostatniej części (Rozdział 10) badano wpływ zastosowania promotorów - tlenku ceru i/lub tlenku cyrkonu. W tym celu przygotowano szereg katalizatorów hydrotalkitowych metodą współstrącania przy stałym pH. Właściwości fizyko-chemiczne przegotowanych materiałów zostały zbadane za pomocą analizy elementarnej (ICP-MS i/lub XRF), dyfrakcji promieni rentgenowskich (XRD), spektroskopii w podczerwieni (FTIR), niskotemperaturowej sorpcji azotu, termo-programowanej redukcji wodorem (H₂-TPR), termo-programowanej desorpcji CO₂ (CO₂-TPD), transmisyjnej mikroskopii elektronowej (TEM), skaningowej mikroskopii elektronowej (SEM) oraz termograwimetrii (TG). Następnie przygotowane katalizatory testowano w reakcji suchego reformingu metanu. Większość testów katalitycznych prowadzono w temperaturze 550°C, która uznawana jest za nisko temperaturę dla procesu DRM. Testy w wyższych temperaturach (650 i 750°) również zostały przeprowadzone dla wybranych próbek. Zastosowanie niskich temperatur reakcji, może być korzystne z ekonomicznego punktu widzenia, w przypadku wprowadzenia procesu na skalę przemysłową.

W celu określenia wpływu metody wprowadzenia niklu do struktury hydrotalkitów, przygotowano cztery próbki katalizatora, do których nikiel został wprowadzony poprzez: (i) współstrącanie w roztworze Na₂CO₃, w wyniku czego wprowadzono nikiel w warstwy brucytowe, (ii) impregnację, dzięki czemu wprowadzono nikiel na powierzchnię katalizatora, (iii) współstrącanie w roztworze kompleksów [Ni(EDTA)]²⁻, skutkującym wprowadzeniem anionów [Ni(EDTA)]²⁻ w przestrzenie międzywarstwowe hydrotalkitu oraz (iv) adsorpcję z roztworu związków kompleksowych [Ni(EDTA)]²⁻, skutkującym wprowadzaniem Ni na powierzchnię materiału

hydrotalkitowego. Ostatnia z wymienionych metod nie została jeszcze opisana w literaturze dotyczącej katalizatorów pochodzenia hydrotalkitowego w reakcji DRM. Charakterystyka przygotowanych próbek katalizatorów potwierdziła skuteczne otrzymanie prekursorów katalizatora. Zawartość niklu w badanych próbkach wynosiła od 0,8% wag. dla próbki otrzymanej za pomocą adsorpcji do ok. 7-8% wag. dla próbek współstrącanych. Najwyższą aktywność katalityczną wykazała próbka impregnowana jonami Ni²⁺, która wykazała stopnie konwersji metanu i CO₂ powyżej 90% w temperaturze 850°C. Tak wysoka aktywność spowodowana była wysokim stopniem dyspersji cząstek niklu. Jednakże najwyższą aktywność w przeliczeniu na gram materiału aktywnego wykazała próbka otrzymana metodą adsorpcji z roztworu kompleksów nikiel-EDTA. Metoda adsorpcyjna skutkowała wprowadzaniem na powierzchnię katalizatora dobrze zdyspergowanych, bardzo małych krystalitów niklu silnie związanych z nośnikiem.

Wpływ zawartości niklu w warstwach brucytowych zbadano przy pomocy próbek katalizatora otrzymanych przez substytucję 5, 15, 25, 50, 75 lub 100% kationów Mg²⁺ przez Ni²⁺ w odniesieniu do naturalnie występującego minerału – hydrotalkit $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. Charakterystyka przygotowanych próbek potwierdziła warstwową budowę materiałów, charakterystyczną dla hydrotalkitu, oraz pożądaną zawartość niklu w warstwach brucytowych, wynoszącą od 3 do ok. 60% wag. Właściwości przygotowanych katalizatorów, takie jak zasadowość, rozmiar krystalitów Ni/NiO, powierzchnia właściwa oraz redukowalność były zależne od zawartości niklu w próbce. Wyniki testów katalitycznych wykazały wysoką aktywność przygotowanych materiałów względem metanu w procesie suchego reformingu metanu, która malała wraz ze spadkiem zawartości niklu w próbce. Ten sam trend wykazywała wielkość krystalitów niklu. Zaobserwowano również wzrost zawartości H₂ w produktach reakcji wraz ze wzrostem zawartości niklu w próbce. Obserwacje te sugerują, że na wartość stopni konwersji CH₄ w reakcji DRM miała wpływ reakcja uboczna – rozkład metanu. Zostało to potwierdzone w osobnych testach katalitycznych. Stopnie konwersji CO₂ nie były zależne w tak dużym stopni od wielkości krystalitów niklu, czyli zawartości niklu w próbce. Były one jednak silnie powiązane z zasadowością badanych układów, szczególnie ze stężeniem silnych centrów zasadowych na powierzchni katalizatora. Najlepszą aktywność katalityczną wykazała próbka otrzymana w wyniku substytucji 25% kationów Mg²⁺ przez Ni²⁺ (zawartość niklu ok. 20%wag). Katalizator ten charakteryzował się najwyższymi stopniami konwersji CO₂, osiągając równowagowe stopnie konwersji CO₂ w temperaturach 650 i 750°C. Wykazał on również stabilną pracę podczas 24h testów stabilności. Można stąd wnioskować, że optymalna zawartość niklu w katalizatorach pochodzących od Ni/Mg/Al materiałów hydrotalkitowych, posiadających stały stosunek $M^{2+}/M^{3+} = 3$, wynosi ok. 20% wag.

Wybrane próbki katalizatorów promowano związkami ceru i/lub cyrkonu. Cer został wprowadzony do układów hydrotalkitowych poprzez adsorpcję z roztworu [Ce(EDTA)]⁻. Cyrkon natomiast wprowadzono w warstwy brucytowe hydrotalkitu, na etapie współstrącania, poprzez częściową substytucję kationów Al³⁺. Obydwa promotory pozytywnie wpłynęły na pracę katalizatora. Wpływ związków ceru był zależny od zawartości niklu w próbce oraz obecności tlenku magnezu. Generalnie, wprowadzenie ceru skutkowało zmniejszeniem temperatury redukcji tlenku niklu, co miało wpływ na wielkość krystalitów Ni oraz typ depozytów węglowych powstałych na powierzchni katalizatora podczas reakcji. Zwiększona stabilność próbek była spowodowana przez inhibicję reakcji rozkładu metanu oraz utlenianie depozytów węglowych w reakcji Boudouarda. Wprowadzenie związków cyrkonu skutkowało wprawdzie obniżeniem stopni konwersji CO₂ i CH₄., ale równocześnie znacznie zwiększyło selektywność procesu względem DRM. Związki cyrkonu spowodowały praktycznie całkowitą eliminację rozkładu metanu. Dodatkowo charakterystyka katalizatorów promowanych cyrkonem po reakcji, wykazała minimalną ilość depozytów węglowych. 24 godzinne testy stabilności próbki promowanej podwójnie związkami ceru i cyrkonu wykazały powolny spadek aktywności w temperaturach 550, 650 i 750°C, jednoznacznie sugerując, że badania w kierunku materiałów hydrotalkitowych zawierających nikiel i promowanych cyrkonem powinny być kontynuowane w celu optymalizacji składu katalizatora, np. stosunku Ce/Zr. Przeprowadzone badania wskazują na bardzo pozytywny wpływ związków cyrkonu na stabilną prace katalizatora.

Résumé de Thèse

L'augmentation des émissions de dioxyde de carbone force l'implémentation de différentes stratégies de réduction des émissions de CO₂ qui peuvent être divisées en deux groupes principaux: (i) Le captage du carbone et stockage (CCS) and (ii) le captage du carbone et utilisation (CCU). Cette dernière approche permet la conversion du CO₂ en un produit à valeur ajoutée créant ainsi un cycle carbone. Il est prédit que dans un future proche, de par l'implémentation des technologies utilisant le CO₂ comme matière première, une nouvelle économie basée sur le dioxyde de carbone sera susceptible de se développer. Un des procédés convertissant le CO₂ en un produit à valeur ajoutée est le reformage à sec du méthane (DRM). Ce procédé produit une quantité importante de H₂ et CO et peut être considéré comme une source attractive pour la production de « syngas », alternative au vaporeformage du méthane. Le DRM possède de nombreux avantages, tel que: (i) la production de syngas avec un rapport H₂/CO plus faible, (ii) il est adapté au procédé Fischer-Tropsch et à la production de composés organiques oxygénés, (iii) il supporte l'idée d'un développement durable par le recyclage du CO₂, (iv) il peut être appliqué pour le transport et le stockage de l'énergie dans un système CETS (Chemical Energy Transmission and/or Storage). Cependant le procédé de DRM n'a pas été commercialisé en raison des taxes « carbone » encore peu dissuasives, de la forte endothermicité de la réaction et par manque de catalyseur actif, stable et bon marché à ce jour.

L'étude de la bibliographie révèle que les systèmes catalytiques les plus efficaces appliqués pour le procédé de DRM doivent être basés sur le nickel comme phase active avec un support mixte composé de magnésium et d'alumininum. Le bénéfice de l'utilisation du Ni vient du fait qu'il s'agit du métal le plus actif dans les réactions de DRM utilisable à l'échelle industrielle. Les catalyseurs basés sur les métaux nobles ont montré une plus forte activité, cependant leur application à grande échelle est limitée en raison de leur prix élevé et faible disponibilité. Par ailleurs, les systèmes catalytiques à base de nickel subissent une désactivation lors de DRM en raison de la formation de dépôt de carbone et par le frittage de la phase active. Dans la bibliographie, différentes stratégies sont proposées afin d'accroitre la stabilité de ces systèmes. Les plus courantes comprennent l'application de supports et/ou de promoteurs à forte basicité afin d'augmenter la capacité d'adsorption du CO₂ et donc l'oxydation des espèces carbonées par réaction inverse de Boudouard, ou en augmentant les interactions entre la phase active de nickel et le support, inhibant ainsi le frittage.

L'application d'un support mixte composé d'oxyde de magnésium et d'oxyde d'alumininum peut traiter ces deux points à la fois, MgO possédant un caractère basique et Ni étant

fortement lié : à MgO par la formation d'une solution solide de MgO-NiO, et à Al_2O_3 dans la phase spinelle NiAl₂O₄.

Les matériaux possédant des propriétés bénéfiques pour la réaction de DRM et pouvant inclure les composants catalyseurs désirés à savoir Ni, MgO et Al₂O₃ sont les hydrotalcites. Les études récentes sur les dérivés de composés hydrotalcites contenant du nickel pour DRM ont montré que ces matériaux sont des catalyseurs très actifs et stables. Par conséquent, l'objectif principal de cette thèse est d'évaluer la performance catalytique de différents systèmes catalytiques à base d'hydrotalcite contenant du nickel lors du reformage à sec du méthane. Une revue de la littérature a montré qu'il existe certains domaines de recherche dans lesquels l'application de dérivés hydrotalcites au reformage du méthane n'avait pas encore été bien étudiée. Le travail effectué pour cette thèse vise donc à combler ces lacunes et celle-dernière a été divisée en trois parties:

- (i) l'influence de l'introduction de nickel dans un système catalytique à base d'hydrotalcite,
- (ii) l'évaluation de la teneur en nickel des couches de brucite de l'hydrotalcite sur les propriétés catalytiques du matériau et
- (iii) l'évaluation de l'effet des promoteurs Ce et/ou Zr.

Afin de répondre à ces problématiques, plusieurs catalyseurs à base d'hydrotalcite ont été synthétisés par la méthode de co-précipitation. Les propriétés physico-chimiques des matériaux préparés ont été évalués au moyen d'analyse élémentaire (XRF ou ICP-MS), XRD, FTIR, N₂-sorption à basse température, H₂-TPR, CO₂-DPT, TEM, expériences SEM et TG. Les matériaux ont ensuite été testés dans la réaction de DRM. La plupart des tests catalytiques ont été effectués à 550°C, ce qui est considéré comme une température plutôt basse pour ce processus, toutefois, l'application de basses températures de réaction est bénéfique sur le plan économique.

Les effets des méthodes d'introduction du nickel ont été évaluées par comparaison de la performance catalytique de quatre catalyseurs dans lequel le nickel a été introduit de manière différente:

- (i) la co-précipitation dans la solution de Na₂CO₃ destinée à l'introduction d'espèces de nickel dans les couches de brucite,
- (ii) la méthode d'imprégnation résultant en l'introduction d'espèces de nickel sur la surface de l'hydrotalcite,
- (iii) la co-précipitation dans la solution de complexes [Ni(EDTA)]²⁻ visant à l'introduction de chélates de nickel dans les espaces inter-couches de l'hydrotalcite et
- (iv) l'adsorption depuis la solution de complexes [Ni(EDTA)]²⁻ visant à l'introduction d'espèces Ni sur la surface de l'hydrotalcite.

Cette dernière technique de préparation du catalyseur pour le DRM n'a jamais été rapportée dans la littérature. La caractérisation des matériaux préparés a révélé que les précurseurs désirés de l'hydrotalcite avaient bien été synthétisés avec succès. La teneur en nickel des échantillons préparés varie de 0,8 à environ 8wt.%. Les propriétés physico-chimiques des catalyseurs dépendent de la méthode d'introduction de nickel. L'activité la plus élevée dans la réaction de DRM a été observée avec l'échantillon préparé par la méthode d'imprégnation, celui-ci présente des conversions de CO₂ et de CH₄ de plus de 90% à 750°C. La plus grande activité de ce catalyseur peut être attribuée à la forte dispersion des espèces de nickel. Toutefois, la plus haute activité par gramme de matériaux actif a été exposée par l'échantillon dans lequel le nickel est introduit par la technique d'adsorption, ce qui peut être attribuée à la formation à la surface du catalyseur de très petits cristallites/agrégats de nickel, très dispersés et fortement liés au support.

L'influence de la teneur en nickel a été étudiée par préparation de précurseurs catalytiques où le nickel est présent dans les couches de brucite. Les différents catalyseurs ont été synthétisés par substitution de 5, 15, 25, 50, 75 ou 100% de Mg²⁺ par du Ni²⁺ dans les couches brucite de l'hydrotalcite minérale naturelle Mg₆Al₂(OH)₁₆CO₃·4H₂O. La caractérisation des matériaux préparés a confirmé la synthèse de matériaux de type hydrotalcite avec la teneur en nickel désirée, qui varie de ca. 3 à 59wt.%. Les propriétés des matériaux, tels que la réductibilité, la basicité, la taille des particules de Ni/NiO ou SBET étaient dépendantes de la teneur en nickel. L'activité des matériaux préparés par rapport à la conversion de méthane est fortement influencée par la taille des particules de Ni, responsable de l'apparition de la décomposition directe du méthane. D'autre part, les conversions de CO₂ ont été principalement affectées par la basicité des matériaux, en particulier par la concentration de sites basiques forts.

La meilleure performance catalytique a été observée avec l'échantillon obtenu par substitution de 25% de Mg²⁺ avec Ni²⁺. Il a montré les plus importantes conversions de CO₂ de tous les échantillons, atteignant les valeurs d'équilibre à 650 et 750°C pour une conversion de méthane la plus élevée. De plus, ce catalyseur a montré une performance stable au cours des tests de stabilité sur 24h. Par conséquent, on peut conclure que la composition optimale pour un catalyseur dérivé d'hydrotalcite à base de Ni/Mg/Al, contenant du nickel dans des couches de brucite, est de l'ordre 20wt.% de Ni pour un rapport M²⁺/M³⁺ de 3.

L'influence des promoteurs Ce et/ou Zr a été évaluée en préparant différents catalyseurs dérivés d'hydrotalcite dans lequel l'oxyde de cérium a été introduit via adsorption depuis une solution de complexes [Ce (EDTA)]⁻, tandis que les cations Zr⁴⁺ ont été introduits dans les couches de type brucite par substitution partielle de cations Al³⁺. Les deux promoteurs ont eu une influence

positive sur la performance des catalyseurs. Les effets de l'ajout de Ce dépendent de la teneur en nickel et de la présence de magnésie dans le catalyseur. De manière général, l'utilisation d'un promoteur Ce a eu une influence sur la réductibilité des espèces de nickel, et ainsi sur la taille des particules de nickel, le type de dépôts de carbone formés lors de la réaction et donc sur la stabilité du catalyseur. La stabilité accrue du matériau a été attribuée à l'inhibition de la réaction de décomposition directe du méthane et l'oxydation des dépôts de carbone par la réaction inverse de Boudouard. L'utilisation d'un promoteur Zr conduit à une diminution l'activité des catalyseurs. Cependant, elle augmente fortement la sélectivité des catalyseurs envers le DRM par inhibition de la décomposition directe du CH₄. De plus, après utilisation, ces catalyseurs présentaient une formation de dépôts de coke minime. Les tests de stabilité sur 24h d'un catalyseur avec promoteur Zr et Ce ont montré une légère diminution de l'activité avec le TOS à 550, 650 et 750°C, ce qui indique qu'il est nécessaire de poursuivre la recherche dans ce domaine afin d'optimiser la composition du catalyseur, par exemple le ratio Ce/Zr. Néanmoins, il semble que le promoteur Zr garantisse un catalyseur dérivé d'hydrotalcite actif et stable pour le DRM.

Academic achievements of the author

Publications concerning PhD Thesis

The results presented in this PhD Thesis were partially published in the following international journals with Impact Factor:

- R.Dębek, A.Gramatyka, M.Motak, T.Grzyebk, P.Da Costa, Produkcja gazu syntezowego w reakcji suchego reforming metanu na katalizatorach hydrotalkitowych, Syngas production by dry reforming of methane over hydrotalcite-derived catalysts – Przemysł Chemiczny 93 (2014) 2026-2032 (IF 0.399)
- 2 R. Dębek, K. Zubek, M. Motak, P. Da Costa, T. Grzybek, Effect of nickel incorporation into hydrotalcite-based catalyst systems for dry reforming of methane, Research on Chemical Intermediates 41 (2015) 9485-9495 (IF 1.221)
- 3 R. Dębek, M. Radlik, M. Motak, M.E. Galvez, W. Turek, P. Da Costa, T. Grzybek, Ni-containing Ce promoted hydrotalicite derived materials as catalysts for methane reforming with carbon dioxide at low temperature – on the effect of basicity, Catalysis Today 257 (2015) 59-65 (IF 3.893)
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- 1. XLV Ogólnopolskie Kolokwium Katalityczne/XLV Polish Annual Conference on Catalysis, 13-15.03.2013, Kraków:
 - Poster: **R.Dębek**, F.Ribeiro, A.Fernandes, M.Motak, Acid-activated, Al-pillared vermiculite as catalyst for dimethyl ether synthesis from methanol, conference materials ISBN 978-83-60514-18-4, p. 69
- 2. Konferencja Naukowo-Techniczna "Sorbenty Mineralne"/Scientific conference 'Mineral Sorbents', 16-18.09.2013 Kraków
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Annex I. Thermodynamics – Gibbs free energy minimization method

Thermodynamic analysis of chemical process involves determination of phase and equilibrium composition of studied system at specific operating conditions. The equilibrium composition of chemical process can be determined by Gibbs free energy minimization method, which was reported to be effective for complex chemical equilibrium problems. The method is based on a fact that the system is thermodynamically favourable when its total Gibbs free energy is at its minimum value and its differential is zero for a given temperature and pressure.

$$(dG^t)_{T,p} = 0 \tag{1}$$

The total Gibbs free energy of the system can be expressed as sum of multiplication products of number of moles of species i times chemical potential of species i:

$$G^t = \sum_{i=1}^N n_i \mu_i \tag{2}$$

where: G^t - total Gibbs free energy; N - total number of species in the reaction system

The chemical potential of a component is given as:

$$\mu_i = \Delta G_{f_i}^0 + RT ln\left(\frac{f_i}{f_i^0}\right)$$
(3)

where: ΔG^{0}_{fi} – standard Gibbs free energy of formation of species i; R – molar gas constant; T – temperature of the system; f_i – fugacity of pure species i; f^{0}_i – fugacity of pure species i at the standard state.

Combinations of equations (2) and (3) results in the expression (4) for total fee energy of the system, which can be minimized for specified temperature, pressure and composition of the system.

$$G^{t} = \sum_{i=1}^{n} n_{i} \Delta G_{i}^{0} = \sum_{i=1}^{n} n_{i} RT ln\left(\frac{f_{i}}{f_{i}^{0}}\right)$$

$$\tag{4}$$