



CO₂ methanation via Nickel based catalysts: on the influence of the supports and the promoters

Chao Sun

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CO₂ methanation via Nickel based catalysts: On the influence of the supports and
the promoters

Méthanation du CO₂ par des catalyseurs à base de Nickel : Effet des Supports et des Promoteurs

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Doctoral thesis in Chemical Engineering-Chemical Technology

Supervised by Prof. Patrick DA COSTA

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Dédicace

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Résumé

Abstract

摘要

Résumé

Les émissions de CO₂ dues aux activités anthropogéniques causent de graves problèmes environnementaux, qui exigent le développement de technologies de réduction du CO₂. L'utilisation chimique du CO₂, en particulier la méthanisation du CO₂ ($\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$, $\Delta H_{298\text{K}} = -165 \text{ kJ/mol}$), offre une voie pour convertir l'excès de CO₂ en gaz naturel synthétique (CH₄) en utilisant des énergies renouvelables. Les métaux de transition, tel que le nickel (Ni), ont été intensivement utilisés pour catalyser la réaction de méthanation du CO₂ grâce à leurs hautes performances, leurs faibles coûts et leur grande accessibilité. Cependant, les catalyseurs à base de nickel rencontrent toujours des problèmes de frittage du métal et de stabilité dans le temps, ce qui limite leur application à grande échelle. Dans ce sens, des recherches se sont concentrées, ces dernières années sur le développement de catalyseurs à base de Ni très actifs et plus stables.

Dans ce but, dans cette thèse, les effets du support et des promoteurs sur la performance des catalyseurs à base de Ni ont été étudiés pour la méthanation du CO₂. Les études ont consisté en la préparation de nouveaux supports avec une structure et une morphologie unique et de catalyseurs supportés dopés par différents promoteurs. Les techniques de caractérisation telles que H₂-TPR, CO₂-TPD, physisorption de N₂, XRD petit angle/grand angle, TEM, HRTEM, EDX, XPS, TGA-MS, TPO, etc. ont été utilisées pour analyser les propriétés des catalyseurs et des supports. Ainsi, l'activité en méthanation a pu être corrélée aux propriétés physico-chimiques.

Tout d'abord, des matériaux à faible coût tels que des catalyseurs Ni-Mg supportés sur de la diatomite et des oxydes mixtes dérivés d'hydrotalcites promus par l'yttrium ont été préparés par la méthode de précipitation-déposition et la méthode de coprécipitation. Leurs activités ont été

étudiées dans la méthanation du CO₂. Ensuite une corrélation entre l'activité et les propriétés physico-chimiques a été proposée.

Dans un second temps, des nanoparticules de CeO₂ ont été synthétisées par la méthode hydrothermique. Celles-ci ont été ensuite imprégnées par des sels de Ni. Les catalyseurs Ni/CeO₂ dopés par différentes charges d'yttrium, ainsi obtenus, ont été étudiés en méthanation du CO₂. La H₂-TPR, l'XPS et les TGA ont confirmé l'augmentation des lacunes d'oxygène sur le support CeO₂ en raison de l'incorporation de Y. En outre, l'augmentation de la charge de Y peut favoriser la formation de « nano tiges » de CeO₂ sur Ni/CeO₂-Y par rapport aux « nano cubes » formés sur le catalyseur Ni/CeO₂, ce qui pourrait expliquer l'augmentation des lacunes d'oxygène et de la surface spécifique. Enfin, la basicité des catalyseurs Ni/CeO₂-Y a également été améliorée grâce à la présence de Y. Enfin, les catalyseurs Ni/CeO₂-Y ont montré des performances catalytiques supérieures à celles du catalyseur Ni/CeO₂.

Enfin, des matériaux mésoporeux ordonnés avec une morphologie unique, tels que des SBA-15 et SBA-16, ont été synthétisés et utilisés pour préparer les catalyseurs Ni/SBA-15 et Ni/SBA-16. Des promoteurs tels que Ce, Y et Ce-Y ont été utilisés pour modifier ces catalyseurs Ni/SBA-15 et Ni/SBA-16. En présence de promoteurs, les performances des catalyseurs Ni/SBA-15 et Ni/SBA-16 ont été améliorées pour la réaction de méthanation du CO₂. Dans ces études, les activités de ces catalyseurs ont été corrélées aux propriétés physico-chimiques.

En un mot, le support peut affecter de manière significative les performances des catalyseurs au Ni dans la méthanisation du CO₂ en raison de sa texture, de sa structure, de sa morphologie, de ses propriétés redox, etc. Le dopage par des promoteurs peut apparemment améliorer l'activité de ces mêmes catalyseurs contenant du Ni et supportés. L'augmentation de leur activité peut être

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corrélée la modification de la basicité, à la taille des cristallites de Ni, à la présence de lacunes d'oxygène et enfin à la morphologie des supports et des catalyseurs finaux.

Mots clés : Méthanation du CO₂, catalyseurs à base de Ni, diatomite, hydrotalcite, CeO₂, yttrium, cérium, Ce-Y, SBA-15, SBA-16.

Abstract

The CO₂ emissions from anthropogenic activities have caused severe environmental problems, which demand the development of CO₂ reduction technologies. CO₂ chemically utilization especially CO₂ methanation ($\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$, $\Delta H_{298\text{K}} = -165 \text{ kJ/mol}$) provides a route to convert the excess CO₂ to synthetic natural gas (CH₄) using renewable energy. Transition metal e.g., Ni has been intensively used to catalyze CO₂ methanation reaction thanks to its high performance, low cost, and high accessibility. Nevertheless, Ni-based catalysts still encounter metal sintering and low stability problems, which limit their large-scale application. In such a case, the development of highly active and stable Ni catalysts has been the research focus.

In this thesis, the effects of support and promoters on the performance of Ni catalysts in CO₂ methanation were studied. The studies consist of the preparation of supports with unique structure and morphology and supported Ni catalysts doped by different promoters. The characterization techniques such as H₂-TPR, CO₂-TPD, N₂ physisorption, small-angle/large-angle XRD, TEM, HRTEM, EDX, XPS, TGA-MS, TPO, etc. were used to analyze the properties of catalysts and supports. Meanwhile, the methanation activity was correlated to the physicochemical properties.

First, the low-cost materials like diatomite-supported Ni-Mg catalysts and LDH derived mixed oxides promoted by yttrium were prepared by the precipitation-deposition method and co-precipitation method, respectively. Afterward, the activities of catalysts were investigated in CO₂ methanation. The correlation between activity and physicochemical properties was investigated.

Secondly, the CeO₂ nanoparticles were synthesized by the hydrothermal method followed by the Ni catalysts prepared by wet impregnation. The Ni/CeO₂ catalysts doped by different loading of yttrium were investigated in CO₂ methanation. The H₂-TPR, XPS, and TGA confirmed the

increased oxygen vacancies over CeO₂ due to the incorporation of Y. Also, the increase of Y loading could promote the formation of CeO₂ nanorods over Ni/CeO₂-Y compared to the nanocubes formed over Ni/CeO₂ catalyst, which could account for the increased oxygen vacancies and surface area. The moderate basicity of Ni/CeO₂-Y catalysts was also improved due to the presence of Y. In the activity test, Ni/CeO₂-Y catalysts performed superior performance compared to Ni/CeO₂ catalyst.

Thirdly, the ordered mesoporous materials with unique morphology e.g, SBA-15 and SBA-16 were synthesized and employed to prepare Ni/SBA-15 and Ni/SBA-16 catalysts. The promoters such as Ce, Y, and Ce-Y were used to modify the Ni/SBA-15 and Ni/SBA-16 catalysts. In the presence of promoters, both Ni/SBA-15 and Ni/SBA-16 catalysts were improved in CO₂ methanation reaction. The activities of such modified catalysts were correlated to the modified physicochemical properties.

In a word, support can significantly affect the performance of Ni catalysts in CO₂ methanation due to their texture, structure, morphology, and redox properties, etc. Doping by promoters can improve the activity of supported Ni catalysts, which are attributed to the modification of basicity, Ni crystal size, oxygen vacancies, and morphology.

Keywords: CO₂ methanation, Ni catalysts, diatomite, hydrotalcite, CeO₂, yttrium, ceria, Ce-Y, SBA-15, SBA-16.

摘要

人类起源的二氧化碳排放已经引起了严重的环境问题，例如全球变暖。这使得开发二氧化碳减排技术变得越来越重要。CO₂的化学利用，尤其是CO₂的甲烷化（ $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$, $\Delta H_{298\text{K}} = -165 \text{ kJ/mol}$ ）提供了使用可再生能源将过量的CO₂转化为合成天然气（CH₄）的技术路径。由于过渡金属镍（Ni）的高性能，低成本和高可获得性等特点，它已经被广泛用于催化CO₂甲烷化反应。然而，Ni基催化剂仍然遭遇金属烧结和低稳定性的等问题，这限制了它们的大规模应用。在这种情况下，开发高活性和高稳定性的Ni催化剂成为了CO₂甲烷化反应的研究重点。

本文研究了载体和助剂对Ni催化剂在CO₂甲烷化反应中性能的影响。这些研究包括制备具有独特结构和形态的载体，以及不同助剂改性的负载型Ni催化剂。使用H₂-TPR，CO₂-TPD，N₂物理吸附，小角/大角XRD，TEM，HRTEM，EDX，XPS，TGA-MS，TPO等表征技术来分析催化剂和载体的性能。同时，催化剂的活性和催化剂的理化性质也被关联起来。

首先，通过沉淀沉积法和共沉淀法分别制备了廉价载体负载的催化剂，如硅藻土负载的Ni-Mg催化剂和稀土元素钇改性的水滑石(LDH)衍生的混合氧化物Ni催化剂。然后，考察了催化剂在CO₂甲烷化反应中的活性。催化剂的活性变化被归于理化性质的改变。

其次，通过水热法合成了CeO₂纳米颗粒。然后用湿浸渍法制备了Ni催化剂。研究了钇对于Ni/CeO₂催化剂在CO₂甲烷化反应中的影响。H₂-TPR，XPS和TGA表征证实了，掺入Y使得CeO₂上的氧空位数量增加。而且，与在Ni/CeO₂上形成的CeO₂纳米方块相比，

Y 的添加可以促进 CeO₂ 纳米棒在 Ni/CeO₂-Y 催化剂上的形成。这解释了催化剂上氧空位和表面积的增加。由于添加 Y，Ni/CeO₂-Y 催化剂的中等强度碱性也增加了。在活性测试中，Ni/CeO₂-Y 催化剂的性能显著优于 Ni/CeO₂ 催化剂。

第三，合成了具有独特形貌的有序介孔材料，例如 SBA-15 和 SBA-16。并用合成的介孔硅材料制备了 Ni/SBA-15 和 Ni/SBA-16 催化剂。同时，使用 Ce，Y 和 Ce-Y 等助剂改性 Ni/SBA-15 和 Ni/SBA-16 催化剂。在助剂改性下，Ni/SBA-15 和 Ni/SBA-16 催化剂在 CO₂ 甲烷化反应中的活性均得到显著改善。这种改性的催化剂的活性与被改变的催化剂的理化性质相关。

总而言之，载体由于其织构，结构，形态和氧化还原特性等，会显著影响 Ni 催化剂在 CO₂ 甲烷化反应中的性能。掺杂助剂可以显著改善负载型 Ni 催化剂的活性，这可以归因于碱性，Ni 晶粒大小，氧空穴数量和形貌的变化。

关键字：CO₂ 甲烷化，Ni 催化剂，硅藻土 (diatomite)，前驱体，水滑石 (hydrotalcite)，钇 (Y)，二氧化铈 (CeO₂)，Ce-Y，SBA-15，SBA-16。



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Chapter I

General Introduction

1. General Introduction

The combustion of fossil fuels and other industrial activities result in abundant emissions of greenhouse gases (GHGs), which consist of carbon dioxide (CO₂), methane and nitrous oxide, etc. CO₂ emission accounts for the majority of the GHGs emissions. The high CO₂ concentration from anthropogenic activities in the atmosphere has resulted in serious environmental problems e.g. global warming. To mitigate the CO₂ emissions, CO₂ capture and storage (CCS) technologies have been developed to capture and store the CO₂ from the atmosphere or industrial sectors. The captured CO₂ can be stored underground or undersea. Besides storage, CO₂ can also be utilized in many ways. The CO₂ capture and utilization (CCU) technologies are developed to use the CO₂ as feedstock to produce valuable products like fuels, chemicals, and materials, etc. The CCU routes like CO₂-Enhanced Oil Recovery Technology (EOR) [1], chemical conversion [2,3], photochemical[4], electrochemical [5], and biochemical process [4], etc. have been widely studied aim to mitigate the CO₂ emission and produce value-added products. Among these routes, the CO₂ chemical utilization methods received intensive attention due to their potential/present industrial application [3]. CO₂ can be converted to methanol, formic acid, formaldehyde, methane, hydrocarbon, higher alcohol, syngas (CO and H₂), etc. by CO₂ hydrogenation [6–11]. The CO₂ hydrogenation to methane or CO₂ methanation is considered the most potent method for CO₂ chemical conversion due to its several advantages.

The CO₂ methanation ($\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$) is a thermodynamic favorable and exothermic reaction [12]. The reaction is favored at a low-temperature range under atmospheric pressure. Also, the high CO₂ conversion and CH₄ selectivity can be reached thermodynamically at moderate conditions. However, good catalytic systems are still needed to catalyze the reaction due to the dynamic barrier. The transition metals-based catalysts e.g. Pd, Rh, Ru, Pt, Ni, and Co were

developed to catalyze the CO₂ methanation reaction. The noble metal-based catalysts such as Rh and Ru showed superior performance at low temperatures. However, the high cost and low availability limit their potential commercialization. In such a case, the Ni-based catalysts had been widely studied as to their low cost, high availability, and comparable activity compared to noble metals-based catalysts [13]. The activity and stability of the Ni-based catalysts depend on the properties of the catalysts such as active metal dispersion, Ni particle size, specific surface area, porosity, redox property, oxygen storage ability, and basicity, etc. As support, promoter, and preparation method have significant effects on the physicochemical properties of Ni-based catalysts, the researches on such aspects have attracted intensive attention to obtain catalysts with high activity and stability.

In this thesis, the different supports like diatomite, hydrotalcite-derived mixed oxides, cerium oxide (CeO₂), and mesoporous silica were used. All these supports were loaded with nickel to be used in the methanation process. Furthermore, promoters such as Y, Ce, and Y-Ce were selected to improve the performance of catalysts in CO₂ methanation.

This doctoral thesis consists of 7 chapters including a General Introduction, the presentation of the State-of-Art concerning the CO₂ Utilization, the Experimental part. The Results start with the presentation of the possible use of Low-Cost Supports for CO₂ Methanation. Then, Y-Promoted Novel Ceria Supported Ni Catalysts for CO₂ Methanation are reported. Moreover, Mesoporous Silica Materials supported Ni catalysts are discussed. Finally, the Conclusion and Prospect are presented.

Thus, in the second chapter, a thorough literature review of the CO₂ utilization routes is made including the comparison of different CO₂ reduction technologies and CO₂ chemical utilization routes are presented. Then Catalysts of CO₂ methanation with Noble metal-based catalytic systems

are discussed. The thermodynamics is then reported. Another sub-chapter deal with Transition metal-based catalytic systems, the Mechanisms of CO₂ methanation. And, finally Assisted catalysis for CO₂ methanation is presented.

The third chapter introduces the experimental parts, which consist of the set-up for catalytic test and a large variety of physicochemical characterizations used to drive the structure-reactivity of the different studied catalysts.

The fourth chapter deals with the low-cost supports prepared Ni catalysts for CO₂ methanation. In detail, the diatomite-supported Ni-Mg catalysts are used to catalyze the reaction. Besides, the mixed oxides derived from layered-double hydroxide-based Ni catalysts are studied in the reaction.

The fifth chapter investigated Y promoted novel ceria supported Ni catalysts for CO₂ methanation. The positive effects of the yttrium are then studied in detail.

The sixth chapter concentrates on two types of mesoporous silica SBA-15 and SBA-16 supported Ni catalysts. The promotion effect is also presented. Thus, the SBA-15 supported Ni catalysts promoted by Ce and Y are introduced. Meanwhile, the SBA-16 supported Ni catalysts doped by Ce or Y are also investigated.

At last, in chapter 7 the conclusion of this thesis is presented and perspectives are reported.

Thus, the aims of this thesis are:

- Investigate the effect of precursors on the performance of Ni-Mg catalysts supported on the low-cost support-diatomite for CO₂ methanation to find a good Ni salt for the preparation of Ni catalyst.
- Study the promotion effect of yttrium on the activity and physicochemical properties of hydrotalcite-derived mixed oxides for CO₂ methanation to establish activity-physicochemical relations on mixed oxides catalysts.
- Design novel Ni/CeO₂ catalysts and investigate the influence of yttrium loading on the performance of Ni/CeO₂-Y catalysts in CO₂ methanation.
- Synthesize mesoporous silica materials and used them as supports of Ni catalysts to investigate the effects of mesoporous silica materials for methanation reaction. The effects of promoters like Ce, Y, and Y-Ce are also studied.

Such results were used to evaluate the effects of support and promoter selections. The important influence of yttrium or ceria was emphasized. And the appropriate content of Y or Ce loading can be found to significantly improve the performance of Ni catalysts. At last, the dual promotion of Y-Ce additives was also demonstrated.



Chapter II

State-of-Art for the CO₂ Utilization

2. State-of-Art for the CO₂ Utilization

2.1 CO₂ emissions and impacts

Since the industrial revolution time, the consumption of energy especially fossil fuels (coal, oil, and natural gas) had been increasing significantly. Although new energy resources e.g. nuclear energy, solar, and hydropower, etc. have been developed to reduce the dependence on fossil energy, Most of the energy consumption is still based on fossil fuels. As shown in Fig.2.1, the primary energy supply from 1971 to 2018 nearly kept stable with the fossil fuels (coal, oil, and natural gas) accounting for the majority part (International Energy Agency, IEA). Meanwhile, the combustion of fossil fuels and other industrial activities resulted in the fast increase of CO₂ concentration in the atmosphere. According to the world meteorological organization (WMO) greenhouse gas bulletin report in 2019, the atmospheric CO₂ concentration has been increasing annually by 2-3 ppm over the last decade [14]. In Fig.2.2, it can be seen that the annual worldwide CO₂ emission has been increasing sharply since the last century and the peak of CO₂ emission has not been reached until 2019. The quick increase of atmospheric CO₂ concentration has caused many severe environmental problems e.g. global warming, climate change, sea level rising, and ocean acidification [15]. In Fig.2.3, it can be seen that the average global temperature has been increasing gradually since the 19th century. The international panel on climate change (IPCC) commission reported that human-induced GHGs emissions had caused the average temperature to increase approximately 1 °C above pre-industrial levels in 2017 and the temperature is increasing at 0.2°C per decade. To mitigate global warming, human society has been taking action to reduce CO₂ emissions. In 2015, the Paris Agreement aimed at reducing the CO₂ emissions had been adopted by 196 parties in which the goal of the agreement is to limit global warming to 1.5 degrees Celsius compared to pre-industrial levels [16]. In order to reach this long-term target, the international

community needs to reach global peaking of GHGs emissions to achieve a climate-neutral world by mid-century. To achieve sustainable development for the human community, many countries have implemented emission reduction policies. For example, China has promised to achieve a carbon-neutral goal in 2060.

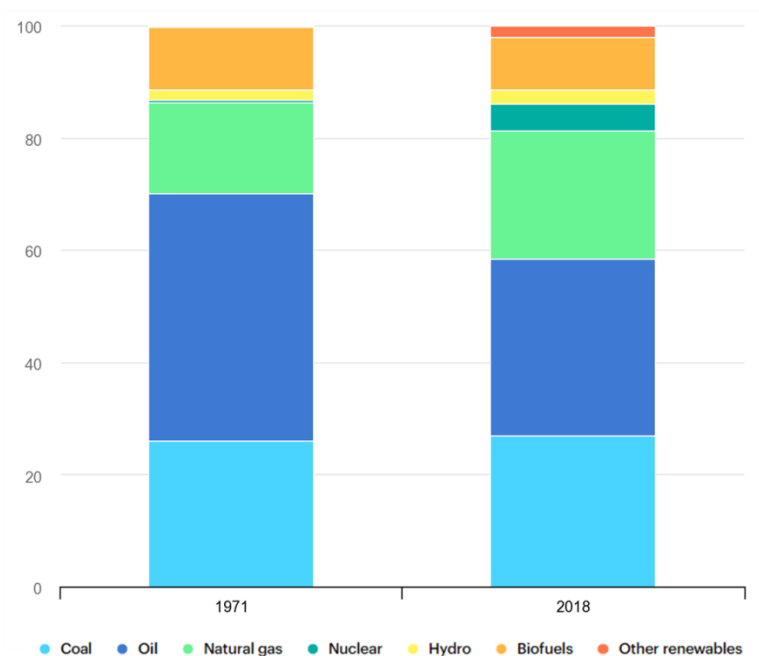


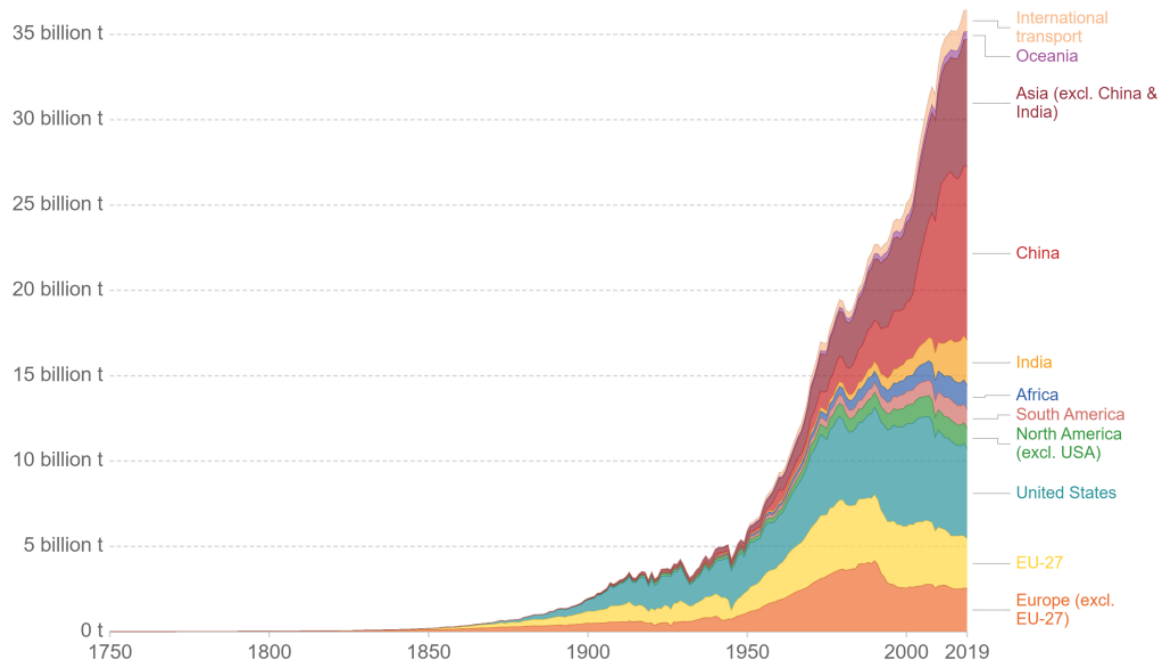
Figure. 2.1. Total primary energy supply by fuel, 1971 and 2018. Adapted from [17].

Regarding the CO₂ emissions reduction, besides limiting the consumption of fossil fuels, the CCS and CCU technologies also help to mitigate the emission. The CCS technology can use the CO₂ capture technology to concentrate the CO₂ and store the resource in geologic ways. The CCU route can use renewable energy to convert CO₂ to valuable resources.

Annual total CO₂ emissions, by world region

This measures CO₂ emissions from fossil fuels and cement production only – land use change is not included.

Our World
in Data



Source: Our World in Data based on the Global Carbon Project
Note: 'Statistical differences' included in the GCP dataset is not included here.

OurWorldInData.org/co2-and-other-greenhouse-gas-emissions • CC BY

Figure. 2.2. Annual total CO₂ emissions by world region. Global Carbon Project; Adapted from [18].

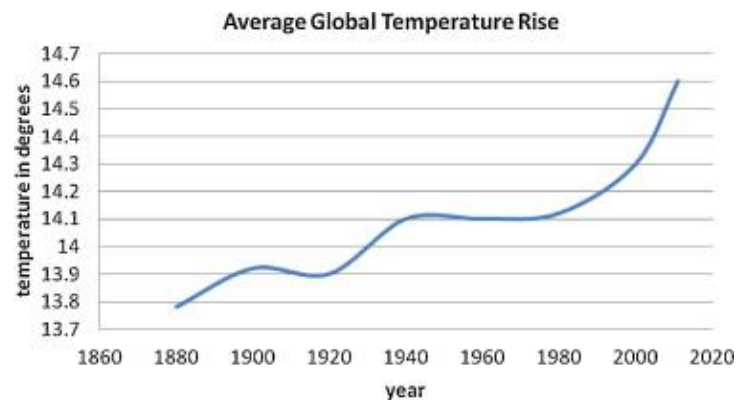


Figure. 2.3. Average global temperature rise, adapted from [15]

2.2 The routes for CO₂ storage and utilization

2.2.1 The CO₂ capture and storage (CCS).

CO₂ sources can be divided into CO₂ point sources and atmospheric CO₂ sources [19]. CO₂ point sources mainly come from the fossil-fueling power plant, petroleum refining, ethylene production, cement production, iron and steel production, ethylene oxide production, hydrogen production, ammonia processing, natural gas processing, and ethanol production chemical plants, paper mills, and fermentation, etc. [20,21]. The CO₂ capture routes consist of capturing CO₂ from the atmosphere i.e. direct air capture (DAC) and CO₂ point sources like the industry sector [21–25].

Fig.2.4 shows a future scenario regarding the capture of CO₂ sources in which the capture from fossil fuels accounts for the overwhelming majority. The CO₂ emissions from the combustion of coal, oil, and gas accounted for nearly half of the fossil fuel CO₂ emissions (30 gigatons annually) or a quarter of the GHGs emissions [22,23]. CO₂ emission from the combustion of fossil fuels including mobile and stationary emissions accounts for 93.74% of the total industrial emissions [21].

For the capture from air, the atmospheric CO₂ can be immobilized by biomass e.g. vegetation, plankton, and algae, etc., or chemical absorbents [22,26]. The direct capture of CO₂ (DAC) by technological systems has been developed and applied in the production of CO₂-free air, which is widely used in the industrial sector e.g. dry ice production and air separation plants [22]. In these routes, the sorbents like sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate (Na₂CO₃), amines are needed to sorb the CO₂ and the captured CO₂ is concentrated for storage (geologic or undersea storage [27]) or recycling. For the strong chemical bases such as NaOH and KOH, their regeneration needs high temperature, which costs abundant energy [22].

The regeneration of amines needs lower temperatures, making them appropriate absorbents. Besides these materials, the novel metal-organic-framework (MOF) materials hybrid ultra-microporous materials (HUMs) were also been used to capture CO₂ [28,29]. Such new materials can serve as physisorbed in DAC, which needs low temperature in the regeneration process [28].

Generally, the purer the CO₂ emission streams are the lower cost the separation systems are. Thus, capturing CO₂ from stationary sites that have purer CO₂ could significantly decrease the cost of the CCS system and improving the economic viability for CCS and climate change mitigation.

A typical CCS system from the power plant diagram is displayed in Fig.2.5. It shows the different components of a CCS system and their consequential effects on electricity production. The CO₂ was captured from the fossil fuel combustion in the power plant followed by compressing and transporting to storage sites e.g., underground or in salts [30,31]. The captured CO₂ can also be directly used in technological applications like dry ice, soft drinks, and supercritical fluid, etc. [1,32,33].

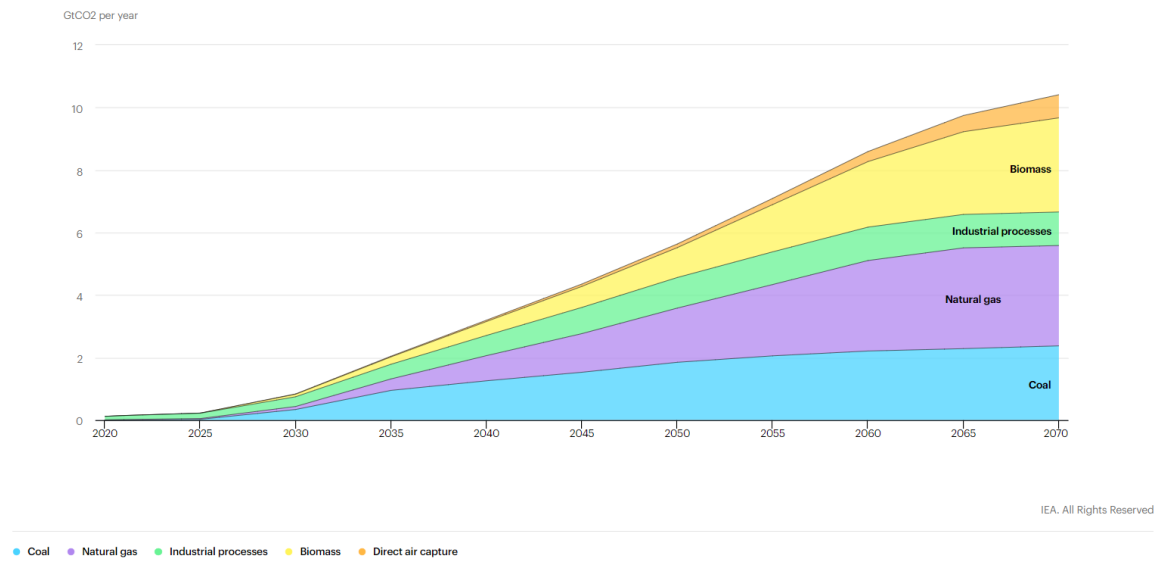


Figure. 2.4. The world captured CO₂ by source in the Sustainable Development Scenario, 2020-2070; IEA, Paris.

Adapted from [34]

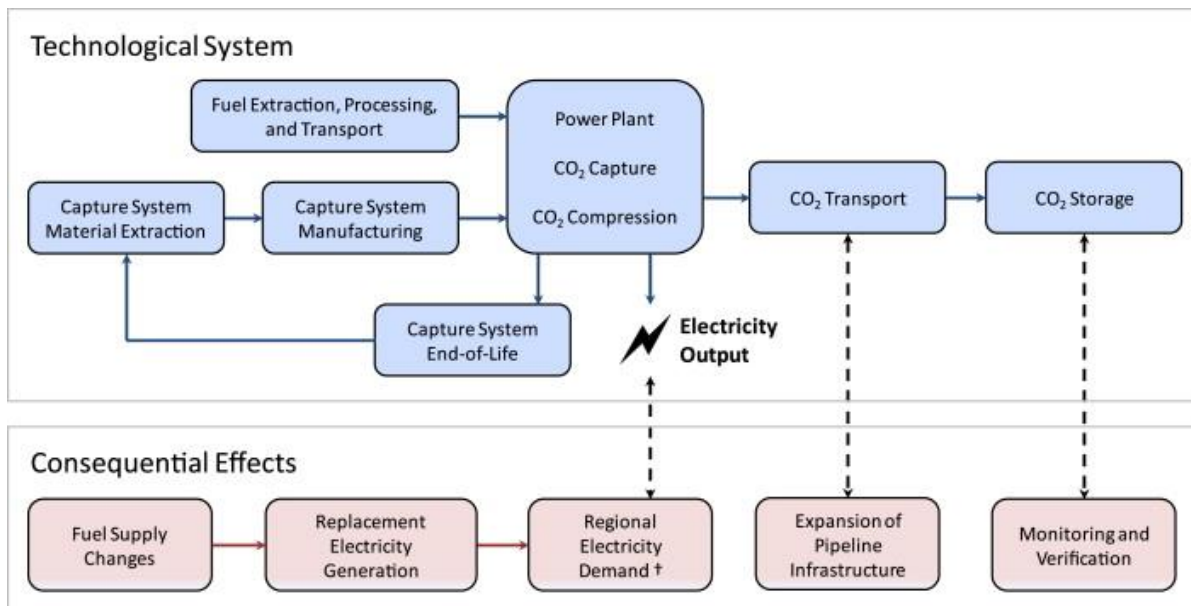


Figure. 2.5. Components of a CCS system, get permission and reproduce from the literature ref. [23]; Elsevier 2012

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2.2.2 The CO₂ capture and utilization (CCU) and why is CO₂ utilization important?

Besides the CCS technology, the CO₂ capture and utilization (CCU) technologies also play very important roles in CO₂ emissions control. The CCS technology normally needs heavy investment especially for the CCS from the air. For example, it will lead to a sharp increase in electricity cost (5-57%) from power plants using CCS [31]. In such cases, the CCU technologies have attracted intensive attention in academic and industrial areas based on their benefits. The CCU technologies can not only help to reduce CO₂ emissions but also produce valuable products.

The CCU route is a technology that uses the captured CO₂ to produce useful fuels, chemicals, and materials [33]. The CO₂ chemical utilization technologies can directly convert the CO₂ to fuels, chemicals, and materials [11,33]. The chemicals like urea, salicylic acid, and inorganic carbonates can be obtained by thermal processes. The chemicals/materials that needed catalytic processes concern the production of formic acid, other carboxylates, organic carbonates, carbamates, acrylates from ethene and CO₂, and products from olefins, dienes, and alkynes reacting with CO₂. The fuel production concentrates on syngas, methanol, higher alcohols, methane, and long-carbon chain hydrocarbon compounds.

In addition to thermal catalysis, electro-catalysis, photo-catalysis, plasma-assisted catalysis, and biochemical routes concerning CO₂ conversion have been also developed [4,35–37]. For instance, the production of biofuel via photocatalysis from microalgae using captured CO₂ seems to be an alternative route [38]. Among these routes, the CO₂ chemical utilization technologies have received the most intensive research interests due to mature technologies and high efficiency [33]. Meanwhile, the other novel approaches are still under research.

Table 2.1 lists various routes towards CO₂ chemical utilization. Six criteria such as Potential development and Economic perspectives, which influence the industrial application of CO₂ utilization technologies, were taken into account. Their degree of development was evaluated by the number from 1 to 4 and colors. The study was from the French Environment and Energy Management Agency (ADEME) [39]. The criteria used to investigate different CO₂ utilization routes were as follow [2,39]:

- Potential development: it indicates the time for the practical industrial facility, which is up to the lab research and development results.
- Economic perspective: it shows the future of obtaining an economic value and reflects the difficulty to achieve economic value.
- External use of energy: it indicates the cost of energy consumption per cost of the product. The energy cost can significantly affect the potential commercialization of the technology, which mainly refers to endothermic processes such as dry methane reforming.
- Potential volume of use of CO₂: it indicates the maximum annual amount of CO₂ that can be transferred by the year 2050.
- Time of sequestration: it refers to the time of CO₂ fixation before it is emitted to the atmosphere.
- Other environmental impacts: they indicate the application of toxic chemicals in the process and hazardous catalysts etc.

Table 2.1 Summary of the different routes in the CO₂ utilization (adapted and modified from [2])

Progress		Potential development	Economic perspectives	External use of energy	Potential volume of CO ₂	Time of CO ₂ sequestration	Impacts on environment
Industrialization	EOR	4	4	3	2	4	4
	Industrial use	4	4	3	2	1.5	4
	Organic synthesis	4	3	2	3	3	3
Short term	Hydrogenation	3	3	2	4	2	3
	Algae open ponds	3	3	4	4	2	4
Medium term	C _x H _y reforming	2	uncertain	1	4	2	1
	Algae reactor	2	2	4	4	2	4
Long term	Mineralization	1	1	1	3	4	3
	Thermochemical	1	2	4	4	2	3
	Electrolysis	1	uncertain	2	4	2	2
	Photo Electro Catalysis	1	uncertain	4	4	2	2
	Biochemical	1	uncertain	4	4	2	3

Potential development: 1, more than 10 years → 4, industrial

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

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

Potential volume of CO₂: 1, less than 10 million tons (Mt) → 4, more than 500 Mt

Time of CO₂ sequestration: 1, very short → 4, long term

Impacts on the environment: 1, significant → 4, low (solvents or toxic chemicals, metal resources)

The CO₂ conversion to fuels can convert CO₂ to energy-rich fuels at the expense of energy.

However, energy consumption today still relies on fossil energy. Thus, the conversion of CO₂ to fuels requires utilizing renewable energy rather than fossil energy for the sake of reducing CO₂ emissions.

CO₂ hydrogenation reactions and CO₂ reforming of methane had been studied intensively thanks to their high feasibility towards application. In these reactions, the H₂ can be produced by water electrolysis or photocatalysis by using renewable energy like solar [40]. Then, the captured CO₂ reacts with H₂ to form fuels like methane or methanol, etc. [41,42]. In these ways, the fluctuant renewable energy can be stored in the form of fuels/chemicals at the expense of CO₂.

2.3 Dry reforming of methane by CO₂

2.3.1 Introduction

The dry reforming of methane reaction (DRM) can convert two types of GHGs to syngas (CO and H₂). The dry reforming of methane ($\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$; $\Delta H_{298\text{K}} = 247 \text{ kJ/mol}$) is an endothermic reaction [43]. The obtained syngas from dry reforming can be used in Fisher-Tropsch synthesis or the production of oxygenated organic compounds [43,44]. However, as the extremely endothermic property of the reaction, it needs a reaction temperature higher than 700 °C to obtain a good conversion of CO₂ and CH₄ in the presence of catalyst [44]. At a low temperature e.g. 450 °C, the conversions of reactants were very low [11]. Meanwhile, the high temperature can result in the sintering of active metal and carbon deposition due to the occurrence of the side reactions, leading to the deactivation of catalyst [43].

The CO/H₂ molar ratio of syngas produced in DRM is close to 1, making the produced syngas appropriate for F-T synthesis. Nevertheless, the RWGS ($\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$; $\Delta H_{298\text{K}} = 41.2 \text{ kJ/mol}$) can result in the molar ratio of CO/H₂ less than 1 [43]. The CH₄ decomposition reaction ($\text{CH}_4 = \text{C(s)} + 2\text{H}_2$; $\Delta H_{298\text{K}} = 75 \text{ kJ/mol}$) and Boudouard reaction ($2\text{CO} = \text{C(s)} + \text{CO}_2$; $\Delta H_{298\text{K}} = -171 \text{ kJ/mol}$) can cause the coking formation on the surface of the catalyst, leading to the

deactivation of the catalyst [43]. Due to the endothermal property and high-temperature operation, the development of DRM catalysts focuses on the catalysts with good activity, high coke resistance, and anti-sintering properties.

Many catalysts e.g. Pt [45], Rh [46], Ru [47], and Ni [11,48–51] had been carried out in the DRM reaction [43]. The noble catalysts like Pt and Rh have a high resistance to coke formation and exhibit high activity and stability. But their high cost and low availability limit the possible large-scale application [52]. On the other hand, the non-noble catalysts like Ni or Co were also developed to catalyze the DRM reaction in which the Ni-based catalysts received extensive research interests [52,53]. The activity and stability of Ni catalysts depend on the properties of active metal, support, and promoters.

The Ni catalysts supported on Al₂O₃ [54], CeO₂ [55], ZrO₂ [56], KIT-6 [50], SBA-15 [57], hydrotalcite [58], etc. were widely studied in DRM reaction. A good dispersion of the active metal leads to the high DRM activity of Ni catalysts. The textural property of the support and the metal-support interaction play important roles in the activity and stability of Ni catalysts. A good selection of support needs to consider the porosity, surface area, robust ability, oxygen vacancies, redox ability, and basicity, etc. [52].

Promoters were also used to improve the activity and stability of the catalysts. The promoters e.g. Y [51,59], Ce [49,51,60], Zr [61,62], La [63], Ce-Zr [62], etc. were investigated in the Ni catalysts for DRM. Li et al. [64] studied the effect of Y₂O₃ on the SBA-15 supported Ni catalysts for DRM reaction. It was found that the adding of Y₂O₃ promoted the dispersion of Ni nanoparticles on the support and enhanced the Ni-support interaction. Thus, high activity and good stability were observed on 9 wt.% Y₂O₃ promoted catalyst. Zhang et al. [65] found that the presence of ceria on Ni/SBA-16 catalyst resulted in the uniformly dispersed Ni particles inside the mesopores and

enhanced Ni-Ce interaction. The adding of ceria results in increased Ce³⁺ concentration and improved structural stability of the catalysts. The DRM test showed that the NiCe/SBA-16 kept stable conversion during the 100 h TOS test.

Apart from the support and promoters, the preparation methods and novel materials were also studied to improve the activity and stability [66,67]. However, the advances in DRM reaction are far from commercialization. The coke deposition is still a major obstacle for industrial applications [52].

2.3.2 Power-to-syngas

The methane reforming reactions can also be integrated into the PtG processes to produce syngas or hydrogen [68,69]. In the power-to-syngas (PtS) concept, the syngas is produced by reverse water gas shift (RWGS) and dry reforming of methane (DRM) reactions powered by renewable energy like solar. The flowcharts of power-to-syngas are displayed in Fig.2.6 in which the power-to-methane route and conventional routes are also displayed. Compared to conventional syngas or synthetic natural gas production, the Power-to-syngas/methane showed less environmental impacts [69]. The PtS process showed more environmental benefits and economic viability than the PtM process under existing conditions [69,70]. However, the PtM process can be more potential if more renewable electricity is used.

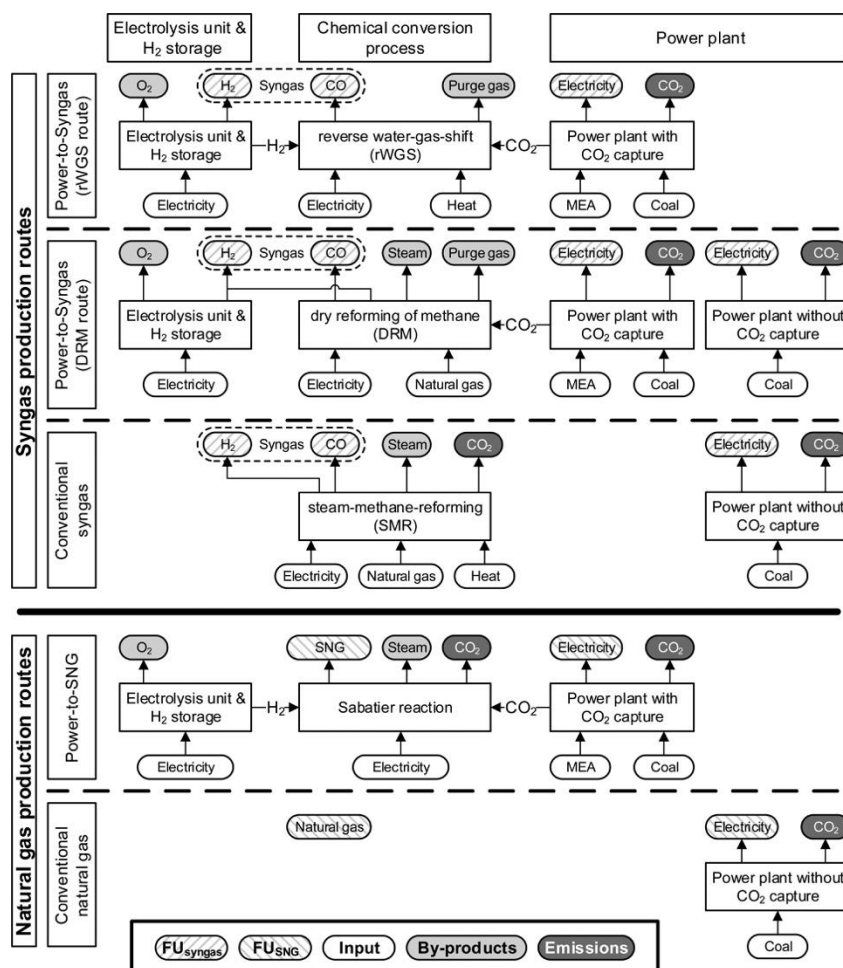


Figure. 2.6. Flowchart of Power-to-Syngas processes (rWGS and DRM) and Power to methane processes as compared with conventional routes; Adapted from [69]

2.4 CO₂ hydrogenation to methanol

2.4.1 Introduction

The CO₂ hydrogenation reactions can produce various chemicals by changing the condition and catalysts [33]. A variety of reactions are shown in Table 2.2. The syntheses of formic acid, methanol, methane, higher alcohols, and higher hydrocarbon are exothermic reactions [8,71–73]. Meanwhile, the formation of formaldehyde and CO is endothermic [72]. Among these reactions,

the CO₂ hydrogenation to methane and methanol attracted intensive interest. In this subchapter, the hydrogenation of CO₂ to methanol is discussed.

Table 2.2. Different CO₂ hydrogenation reactions.

Number	Reaction Formula	Product
(1)	$\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}$	Formic acid
(2)	$\text{CO}_2 + 2\text{H}_2 \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O}$	formaldehyde
(3)	$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	methanol
(4)	$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	methane
(5)	$\text{CO}_2 + \text{H}_2 \rightarrow \text{C}_n\text{H}_m + \text{H}_2\text{O}$	hydrocarbon
(6)	$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$	Reverse-water-gas-shift
(7)	$\text{CO}_2 + \text{H}_2 \rightarrow \text{C}_n\text{H}_m\text{OH} + \text{H}_2\text{O}$	Higher alcohol

The reactions involved in CO₂ hydrogenation to methanol were listed in Table 2.3. It can be seen from Table 2.3 that both the CO₂ methanolization and CO methanolization are exothermic reactions, which are favored at low temperatures. The reverse water-gas-shift reaction, which is endothermic, also exists in the CO₂ hydrogenation to methanol process [74]. From the thermodynamic calculation results of CO₂ methanolization, the reaction is favored at low temperature, high pressure, and high H₂/CO₂ ratio [74]. However, the actual CO₂ methanolization reaction also generally needs a temperature of higher than 50 °C and the presence of an appropriate catalyst [75]. Even in harsh conditions, the CO₂ conversion and CH₃OH selectivity were still very low [75].

Table 2.3. Reactions involved in CO₂ hydrogenation to methanol process

Type	Formula	ΔH_{298K} (kJ·mol ⁻¹)	Definition
1	$\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-49.4	CO ₂ methanolization
2	$\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$	-90.4	CO methanolization
3	$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$	41.0	Reverse water-gas shift

Methanol can be used as fuel directly for transportation or act as a chemical feedstock. CO₂ hydrogenation to methanol technology can not only alleviate the CO₂ emissions but also produce value-added methanol. The heterogeneous catalysis on this reaction received intensive research interests. The catalytic systems mainly consist of transition metal-based catalysts and main group metal-based catalysts. The transition metal-based catalysts mainly focus on Cu-based catalyst and noble metal-based catalyst e.g., Pt and Pd [76–78]. Meanwhile, the main group of metal-based catalysts is made up of In₂O₃ catalysts and Ga-based catalysts [79,80]. Among them, the Cu-based catalyst was regarded as the most potential candidate for industrial application due to the low cost and high availability.

The studies for Cu-based catalysts mostly focused on the active sites of catalyst, the effect of catalyst structure, and activation and deactivation mechanisms [74]. It was found that the synergistic effect between Cu and ZnO contributed to the formation of methanol over Cu/ZnO/Al₂O₃ catalyst in CO₂ hydrogenation to methanol, in which the formate was considered as the reaction intermediate [76]. Sittichai et al. [81] studied the active sites of Cu catalysts in methanol synthesis. The XPS characterization revealed that only metallic Cu species existed on the surface of the catalysts. The Cu⁰ particle size and ZnO crystallinity were directly linked with the activity of such catalysts. Smaller Cu particles resulted in a higher TOF value in methanol

production. The Cu-ZnO synergy was also a key parameter for the methanol formation. Also, the Cu structure was demonstrated to be an important factor in methanol synthesis [74]. Thus Cu atomic plane can affect the catalytic activity of Cu catalysts in methanol synthesis in which the Cu(110) orientation plane was found more active in methanol formation rate compared to that on Cu(100) and polycrystalline copper, indicating the structural sensitivity of Cu catalysts [82]. Over the time on stream (TOS) process, as for methanation, a deactivation can occur for methanolization reaction. Thus, on Cu/ZnO/Al₂O₃ catalyst after a long TOS run, the agglomeration of ZnO particles and partial oxidation of metallic Cu were observed and were presented as key parameters for the deactivation of the studied catalysts in methanol synthesis [83].

Furthermore, to improve the catalytic performance of catalysts in CO₂ hydrogenation to methanol reaction, intensive research had been done regarding promoters, support, and preparation methods. Alkali and alkaline earth oxides had been reported to have a positive effect on Cu catalysts in methanol production [84]. It was found that the Ba promoter can improve the activity of Cu/Al₂O₃ catalyst towards methanol synthesis while the potassium (K) promoter prefers to RWGS reaction [84]. Support oxides such as Al₂O₃, ZrO₂, Ga₂O₃, and Cr₂O₃ were also used as modifiers or promoters for Cu/ZnO catalysts [85]. The other studies on additives mainly concentrate on the study of rare earth oxides (La or Ce) [86], amphoteric oxides (e.g., TiO₂ and ZrO₂) [87], noble metal like Ag or Au [88,89], main group oxides (e.g., SiO₂) [90], and materials with semiconductor properties e.g., g-C₃N₄, etc. [91].

Regarding support, metal oxides like Al₂O₃, ZrO₂, CeO₂, and SiO₂ are then the most studied materials. The properties of the support, which consist of texture, structure, acidity/basicity, and electronic property, can have a significant effect on the performance of the catalyst [74]. Moreover, it has been reported that the porosity of the support with ordered or unordered porosities can

significantly affect the stability of for example CuZnO/SiO₂ methanol synthesis catalysts [92]. The narrowest pore constrictions of the support can mitigate the growth of metal particle size and improve catalyst stability. The other materials such as layered double hydroxides (LDHs) and carbon nanotubes (CNTs) also receive more attention recently.

The preparation method can change the catalyst structure and distribution of active sites over methanol synthesis catalysts. The most common method is the precipitation method, which allows high metal loadings and well-defined metal particles. Other methods such as the sol-gel method, liquid reduction, ammonia evaporation, microwave, and combustion method, etc. were also studied in these years [74,93,94].

Although many efforts have been devoted to the development of methanol synthesis catalysts, the activity and yield of methanol are still not very high due to the thermodynamic and dynamic barrier.

2.4.2 Power-to-methanol systems

The conventional methanol synthesis consists of the coal gasification and subsequent syngas to methanol reaction. However, this route results in severe environmental problems like CO₂ emission and sulfur pollutants [95]. Therefore, the low carbon synthesis of methanol was studied to replace the conventional way. The CO₂ hydrogenation to methanol route using solar energy attracted intensive attention due to its economic and environmental performance. For example, the solar energy-biomass-assisted CO₂ hydrogenation to methanol system can reduce the environmental impacts to 57.5% compared to that of coal gasification system [95]. As displayed in Fig.2.7, the system uses the CO₂ from the biomass power plant and H₂ from biomass combined with the solar power plant to produce methanol. However, the cost of methanol by this system is

5 times more than that of coal gasification way. Thus, the studies focus on decreasing the cost of photovoltaic electricity and improving the efficiency of water electrolysis [95].

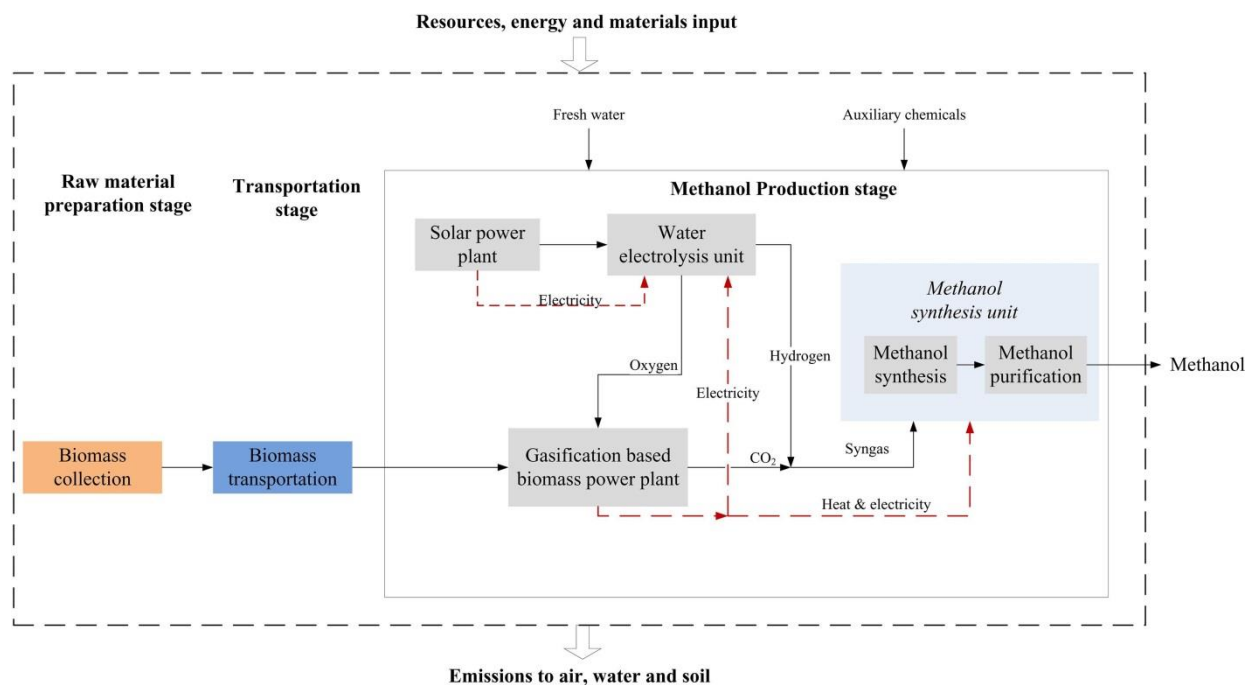


Figure. 2.7. Diagram of solar energy-biomass assisted CO₂ hydrogenation to methanol system; adapted from [95]

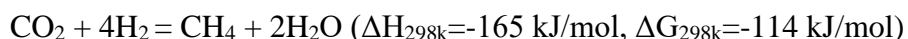
Liquid sunshine is a concept that uses solar energy to chemically synthesize liquid fuels e.g. methanol [96]. Methanol can be used as vehicle fuel [97]. The studies on this topic hope to produce clean energy as an alternative fuel. Regarding the application possibilities, the large-scale liquid sunshine project was tested in China in 2020.

Although many benefits of methanol, until now, the methanol production from CO₂ hydrogenation using solar energy still encounters high capital cost and running cost. Thus, the power-to-gas e.g. syngas and methane routes have attracted intensive attention.

2.5 CO₂ methanation

2.5.1 Introduction

CO₂ methanation, also known as Sabatier reaction, was found by Paul Sabatier [98].



This reaction is thermodynamically favorable and exothermic. Thus, this reaction can be carried out in moderate conditions with a high CO₂ conversion [99]. Also, the produced methane can be transported by established pipeline systems. This technology can be used in the Renewable Power-to-Gas (PtG) concept, which uses renewable energy to convert CO₂ to CH₄ [100]. By this route, the fluctuant renewable energy e.g. wind, solar, and hydropower can be stored in the form of CH₄ by PtG route.

The CO₂ reduction to CH₄ pathways consists of thermochemical, electrochemical, photochemical, and biological conversion processes [99,101]. The thermal catalysis of CO₂ reduction received the most intensive research attention because of the mild reaction condition, simple reaction set-up, high activity, and high feasibility towards commercialization. The other pathways are still under research period. The catalytic low-temperature CO₂ methanation is regarded as a potential route towards the large-scale application of CCU.

Although the CO₂ methanation reaction can reach a high activity and selectivity of CH₄ at low temperature in the thermodynamic simulation process, it needs the presence of appropriate catalytic systems under practical conditions due to the existence of a dynamic barrier. Thus, the presence of catalysts is indispensable in this reaction. The VIII group transition metal-based catalysts e.g. Pd [102–104], Rh [105–110], Ru [111–118], Pt [119,120], Fe [109,121], Co [122–129], and Ni [130,131,140–144,132–139] have been developed by scientists to catalyze the

reaction. For noble metal-based catalysts, the Ru and Ru-based catalysts generally showed superior activity. The studies regarding TiO₂ supported catalysts found that the CO₂ conversion or turnover frequency (TOF) followed the order of Rh>Ru>Pt>Pd [145]. The noble metal-based catalysts can catalyze the reaction at low temperatures (<200 °C) under atmospheric pressure [102,106,146]. The studies on Rh/ γ -Al₂O₃ catalyst for CO₂ methanation found that the reaction could happen at as low as 100 °C with nearly 100% of CH₄ selectivity [106]. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results confirmed that the CO was the main intermediate during the reaction[106].

As the high cost and low availability of noble metals, the potential commercialization of the CO₂ methanation needs to find materials that possess the properties such as low cost, high availability, high activity, and CH₄ selectivity as well as high stability. In such a case, the other transition metals e.g. Co and Ni have attracted more attention both in academic and commercial aspects [147].

2.5.2 Thermodynamic aspects of CO₂ methanation

2.5.2.1. The effect of temperature in CO₂ methanation simulation

The effects of temperature towards CO₂ conversion and CH₄ selectivity in CO₂ methanation were simulated by the HSC Chemistry 5.0 software using the Gibbs free energy minimization method. The CO₂ conversion and CH₄ selectivity are calculated following Equation (1) and (2):

$$X_{CO_2}(\%) = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100\% \quad (1)$$

$$S_{CH_4}(\%) = \frac{F_{CH_4,out}}{F_{CO_2,in} - F_{CO_2,out}} \times 100\% \quad (2)$$

The X_{CO_2} and S_{CH_4} represent the CO₂ conversion and CH₄ selectivity. The $F_{\text{CO}_2,\text{in}}$, $F_{\text{CO}_2,\text{out}}$, and $F_{\text{CH}_4,\text{out}}$ represent the molar flow of CO₂ or CH₄ in which the “in” and “out” mean inlet and outlet, respectively.

The possible reactions in CO₂ methanation reactions were displayed in Table 2.4. We can List eight reactions that probably happened during the CO₂ methanation process. Two of them are endothermic reactions and 6 reactions are exothermic thermodynamically.

The results of the effect of temperature at 1 bar in methanation were displayed in Fig.2.8. The molar ratio of H₂/CO₂ was controlled at 4 with a gas hourly space velocity (GHSV) of 12,000. As shown in Fig.2.8a, the CO₂ conversion decreases with the increase of temperature until 839 K and then increases gradually at atmospheric pressure. As displayed in Table 2.4, the methanation reaction is an exothermic reaction, which is favored under low temperatures. In Fig.2.8b, the CH₄ selectivity decreases gradually with the increase of temperature up to 773 K and then decreases sharply until nearly zero. Meanwhile, the selectivity of CO increases to nearly 100% as the temperature increasing up to 1173 K. The presence of CO, which is the main by-product in methanation reaction, was caused by the reversed water gas shift reaction (Table 2.4, $\text{CO}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{CO}$) [148].

Table 2.4. Reactions involved in the CO₂ methanation process.

Type	Formula	ΔH_{298K} (kJ·mol ⁻¹)	Definition
1	$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$	-165.0	CO ₂ methanation
2	$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$	41.2	Reverse water-gas shift
3	$\text{CO}_2 + 2\text{H}_2 = \text{C} + 2\text{H}_2\text{O}$	-90.1	CO ₂ reduction
4	$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$	-206.2	CO methanation
5	$2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$	-247.3	Reverse CH ₄ dry reforming
6	$2\text{CO} = \text{C} + \text{CO}_2$	-172.4	Boudouard reaction
7	$\text{CO} + \text{H}_2 = \text{C} + \text{H}_2\text{O}$	-131.3	CO reduction
8	$\text{CH}_4 = 2\text{H}_2 + \text{C}$	74.8	CH ₄ cracking

The molar ratio changes of the species were shown in Fig.2.8c. It can be seen from Fig.2.8c that the molar fraction of CH₄ decreases to nearly zero as the temperature increases up to 973 K and then keep stable. A similar evolution trend is also found over the molar fraction of H₂O, with a molar ratio of 12% found after 973 K. The change in the concentration of CH₄ and H₂O with the increase of temperature also proves that methanation reaction is favored in low temperature. The molar fraction of CO₂ increases gradually up to 823 K and then decreases with the increase of temperature. The concentration trends of H₂ and CO experience a slow, sharp, and stable increasing trend individually during the temperature range. In the calculation, nearly no carbon was formed in the chosen conditions. As reported by Jung-Nam Park [103], the methanation reaction may experience the route CO, in which CO is the main intermediate, in which the CO₂ reacts with H₂ to produce CO by reverse water gas shift, and the CH₄ is formed by CO methanation [148]. The thermodynamic results reveal that the reaction temperature should not be very high to reach a high CO₂ conversion at ambient pressure. However, the kinetic barriers determine that the

CO₂ activation is too difficult at low temperatures, which means the presence of an appropriate catalyst is necessary for the reaction to take place [148,149].

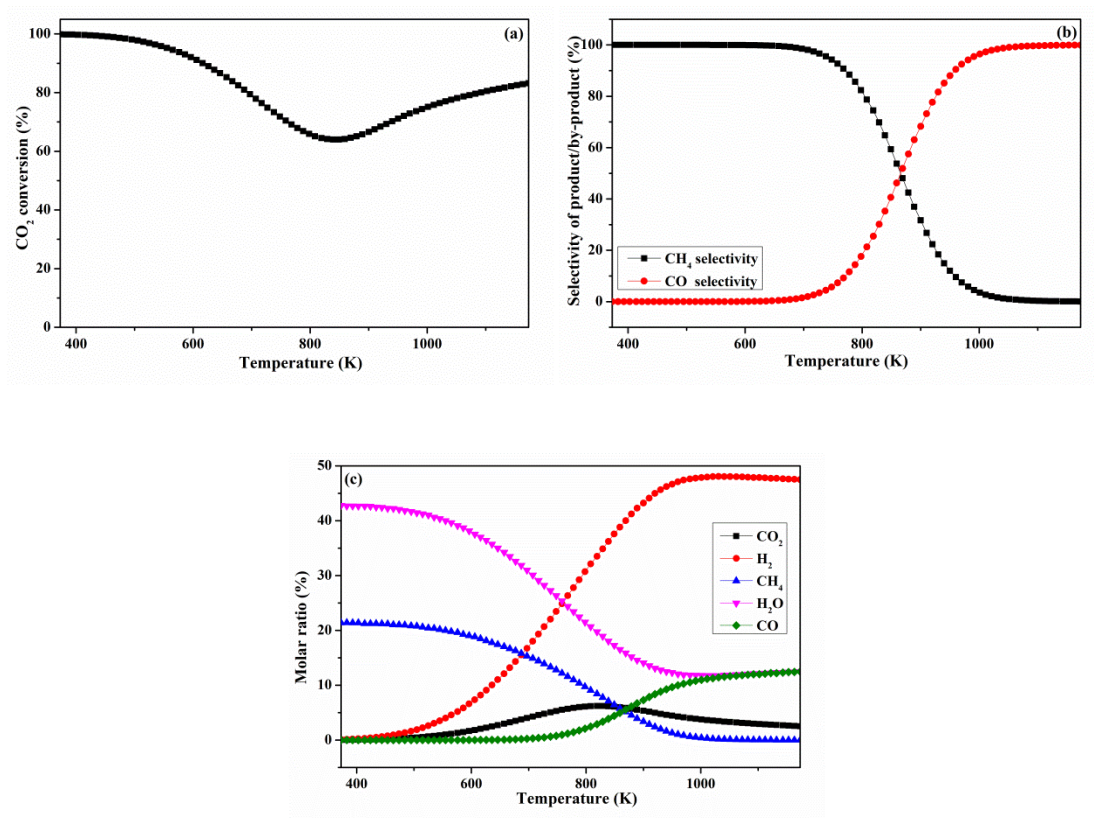


Figure. 2.8. Effect of temperature on CO₂ conversion (a), CH₄/CO selectivity (b), and molar ratio of specie (c) in methanation; Condition: 1 bar, H₂/CO₂/Ar (molar ratio)=60/15/25, GHSV=12,000 h⁻¹ [141,142].

2.5.2.2. The effect of the pressure in CO₂ methanation

The thermodynamic effect of the Pressure on CO₂ conversion and CH₄ selectivity in CO₂ methanation were calculated and displayed in Fig.2.9. As shown in Fig.2.9a, the CO₂ conversion at each pressure presents a gradually decreasing trend below 873 K. The increase of pressure causes the increase of CO₂ conversion because the CO₂ methanation reaction is a volume reducing

reaction, with the gas volume changing from 5 to 3 units. Thus, the increase of pressure can promote the reaction thermodynamically. However, when the reaction temperature exceeds 873 K at 1 bar, the CO₂ starts to be converted through the reverse water-gas-shift reaction (Table 2.4, $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$) dominates the reaction [148]. The effect on CH₄ selectivity is shown in Fig.2.9b. It is found that the CH₄ selectivity decreases slowly when the temperature increases until 773 K because of the exothermicity of methanation. Beyond 773 K, the sharp decrease of CH₄ selectivity is registered at each pressure, which is attributed to the effect of reverse water-gas-shift reaction. However, the increase of pressure can significantly promote the CH₄ selectivity, which is attributed to the volume reducing property of methanation. Meanwhile, no carbon was registered in the studied pressure range. This can be explained by the effect of H₂O formed in the reaction, which can suppress the formation of coke [148].

The calculation results in this study are well consistent with the calculation results carried out elsewhere [106,148,150].

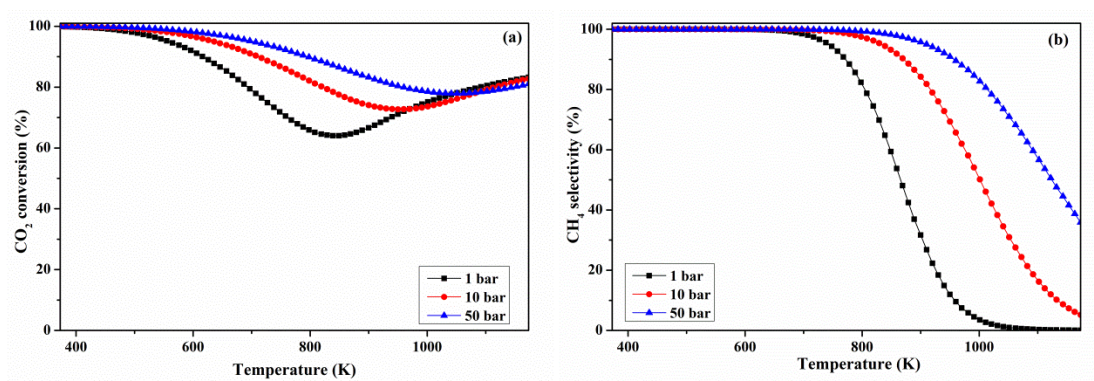


Figure. 2.9. Effect of pressure on CO₂ conversion (a) and CH₄ selectivity (b) in methanation; Condition: H₂/CO₂/Ar (molar ratio)=60/15/25, GHSV=12,000 h⁻¹

2.5.2.3. The effect of H₂/CO₂ ratio in CO₂ methanation simulation

The effect of the H₂/CO₂ ratio on methanation reaction was calculated and shown in Fig.2.10. It can be seen from Fig.2.10a that the H₂/CO₂ ratio notably affects the CO₂ conversion. The increase in H₂/CO₂ ratio leads to a significant increase in CO₂ conversion. The same phenomenon is also found for CH₄ selectivity. In the case of the H₂/CO₂ ratio being 2, the CO₂ conversion and CH₄ selectivity are just 75% and 30%, separately. Meanwhile, the CO₂ conversion and CH₄ selectivity are nearly 100% when H₂/CO₂ ratio reaches 4. A lot of carbon was formed below 773 K when the H₂/CO₂ ratio is 2. Almost no carbon deposition is registered when the H₂/CO₂ ratio exceeds 2. The CO₂ reduction reaction (Table 2.4, $\text{CO}_2 + 2\text{H}_2 = \text{C} + 2\text{H}_2\text{O}$) appeared when the H₂/CO₂ ratio is 2, which results in the abundant formation of carbon.

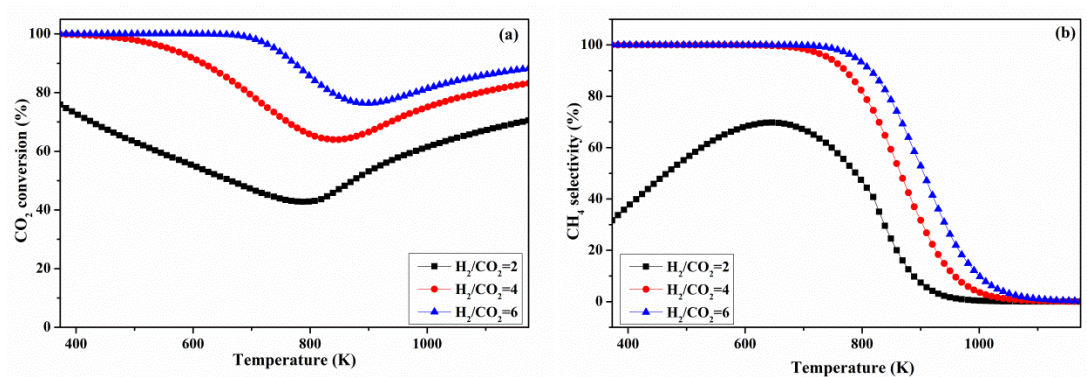


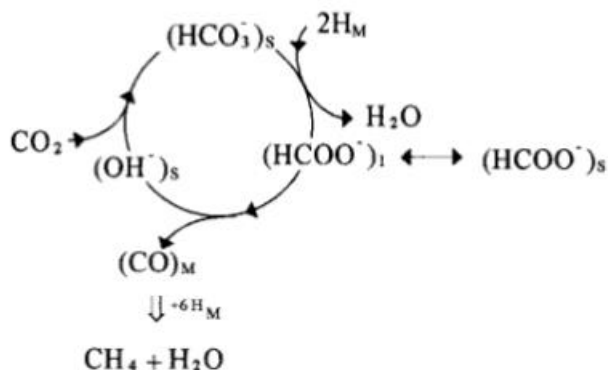
Figure. 2.10. Effect of H₂/CO₂ ratio on CO₂ conversion (a) and CH₄ selectivity (b) in methanation; Condition: 1 bar,

GHSV=12,000 h⁻¹

2.5.3 Mechanisms of CO₂ methanation

2.5.3.1 The CO as intermediate of CO₂ hydrogenation mechanism

Nowadays the mechanism of CO₂ methanation remains unclear. Regarding the intermediate that account for the formation of methane, there are mainly two mechanisms proposed [151]. One of them is the mechanism that carbon oxide plays as an intermediate in which CO₂ is reduced to CO and subsequently the methane is produced by CO methanation [152]. The density functional theory on Ni(111) surfaces proposed three mechanisms in which the mechanism with a rate-determining step of CO → C + O has the lowest energy barrier [153]. The diagram of the scheme is shown in Scheme 1.

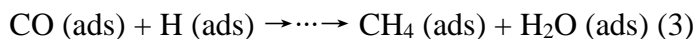
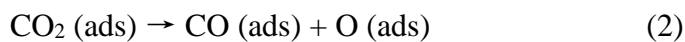


Scheme 1. Mechanism of CO₂ methanation with CO as an intermediate (M: metal, S: support); Reproduced with permission from ref [154]. Copyright Elsevier 1997.

The experimental studies on the Ni catalysts supported on activated carbon for CO₂ methanation also confirmed that the CO was an indispensable intermediate in the formation process of methane [152].

Zhou et al. [155] studied the effect of TiO₂ structure on Ni/TiO₂ for CO₂ methanation. The methanation over Ni/TiO₂ catalyst with principle Ni (111) facet experienced the CO intermediate pathway. However, the catalyst with multi-planes of Ni followed the mechanism of formate species as an intermediate pathway in which the Ni only accounted for H₂ dissociation.

The mechanism study on the noble metal-based catalyst (Rh/ γ -Al₂O₃) at low temperature and ambient pressure revealed that the methanation process followed the pathway without the formation of formate species [156,157]. Three steps can be listed as follows:



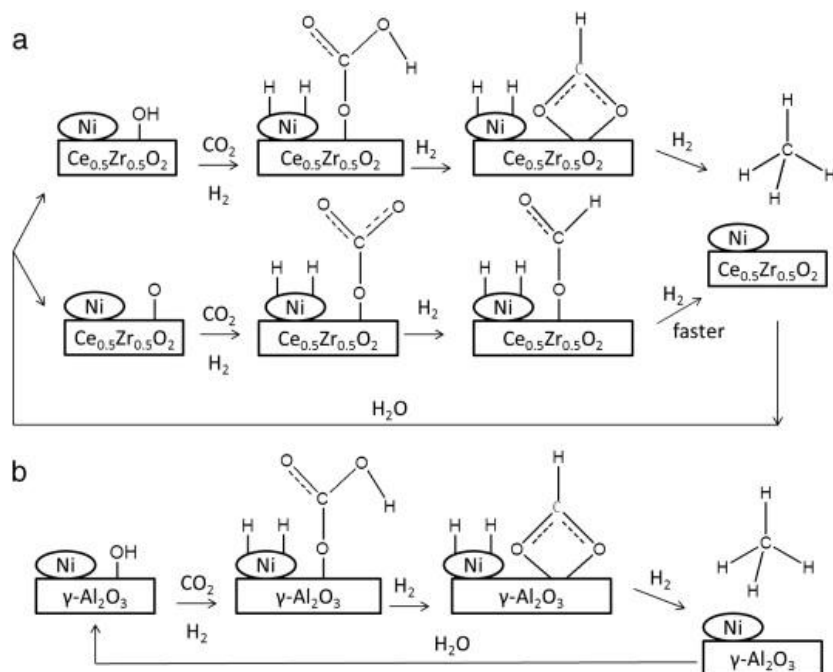
The H(ads) species were formed in the dissociation process of H₂. However, it was also noted that CO₂ adsorption could be a complicated process [157]. The oxidation of part of rhodium particles was also registered, which was attributed to its oxidation by O(ads).

2.5.3.2 The formate intermediate mechanism

The other proposed mechanism involves the formation of formate species during the reaction; this latter species is subsequently hydrogenated to methane [158,159]. This mechanism needs both the participation of support and active metal. It was reported that many intermediates e.g., hydrogen carbonate, bidentate carbonate, monodentate carbonate, bridged carbonate, formate, and nickel carbonyl hydride can be formed [158]. The properties of support can affect the variety of intermediates. As presented in Scheme 2 for the mechanism over Ni/Ce_{0.5}Zr_{0.5}O₂ and Ni/ γ -Al₂O₃ catalysts, the H₂ gas is adsorbed and dissociated on the surface of the Ni atom to produce H while

the CO₂ molecules are adsorbed and dissociated on the support surface to form carbonate species. The carbonate (bidentate or monodentate) and hydrocarbonate species subsequently react with the H to form formate (bidentate or monodentate) species, which will be hydrogenated by H to produced methane as reported elsewhere [158]. For the Ni/ γ -Al₂O₃ catalyst, it was demonstrated by FTIR that more hydrogen carbonates formed over the catalyst [160]. The hydrogen carbonate species were hydrogenated to bidentate formate species, which were hydrogenated to methane. For Ni/Ce_{0.5}Zr_{0.5}O₂ catalyst, more monodentate carbonate rather than hydrogen carbonate species formed, thus leading to more monodentate formate species, which were hydrogenated to methane. The pathway of methane formation over Ni/Ce_{0.5}Zr_{0.5}O₂ is faster than that over Ni/ γ -Al₂O₃ catalyst [160]. This latter result is attributed to the difference of basicity, in which more medium basic sites over Ni/Ce_{0.5}Zr_{0.5}O₂ are favorable for the formation of monodentate carbonate.

Another important parameter is the nickel particle size. In the literature, the study on the effect of Ni particle size over Ni/SiO₂ catalysts showed that the particle size of Ni also had significant effects on the pathway of methane formation [161].



Scheme 2. Proposed mechanisms over Ni/Ce_{0.5}Zr_{0.5}O₂ and Ni/γ-Al₂O₃ catalysts; Reproduced with permission from ref. [160]; Copyright Elsevier 2014.

2.5.3.3 On the important presence of side reactions in CO₂ methanation reaction

In the thermodynamic analyses of CO₂ methanation, it has been demonstrated that the species formed during the methanation process depend significantly on the reaction conditions. Under atmospheric pressure, the main by-product in thermodynamic analyses is carbon monoxide (CO), which originates from the RWGS reaction ($\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) or reforming reactions [48,161]. Besides, the CO species can also be formed by the hydrogenation of formate species as intermediates [161]. The presence of CO can also cause the sintering of active metals (Ni, etc.), which is caused by the formation of Ni(CO)_x species, leading to the agglomeration of Ni particles [162].

The H₂O formed in methanation reaction can induce the formation of Ni-hydroxide at low temperature, which results in the consequent decrease of metallic nickel. The Ni-hydroxide species cannot be reduced to Ni metal fast and contribute to the sintering of Ni and the formation of hardly reducible Ni-aluminate, leading to partial deactivation of catalysts [163].

When the ratio H₂/CO₂ decreases, the carbon can also be formed due to parallel reactions such as the Boudouard reaction or/and CO₂ reduction. It is worth noting that carbon deposition also occurs at high pressure over some catalytic systems [121].

2.5.4 The catalysts for CO₂ methanation

2.5.4.1 Noble metal-based catalysts

The noble metal-based catalysts such as Pt [145], Rh [107], Ru [118,164,165], and Pd [103,104] were also studied in CO₂ methanation. Table 2.5 summarized some noble-metal-based catalysts as compared to transition metal catalysts in CO₂ methanation. The noble metal-based catalysts could be very active at low temperatures.

Paraskevi et al. [145] studied the catalytic performance of supported noble metal-based catalysts for CO₂ methanation. It was then showed that the CO₂ conversion of TiO₂ supported noble metal catalysts decreased following the order Rh>Ru>Pt>Pd, with the Rh/TiO₂ catalyst having the higher activity and selectivity of CH₄. The Pt and Pd catalysts were mainly known to promote the RWGS reaction to produce CO. The Ru crystallite size had a significant effect on the performance of Ru/TiO₂ and Ru/Al₂O₃ catalysts for CO₂ methanation. Also, the CO acted as an important intermediate for Ru catalysts during the formation of methane [145].

For noble metal-based catalysts, the CO₂ methanation is known to be structure sensitive reaction, which means the metal crystallite size has significant effects on the performance of the catalysts. The investigation of Rh/ γ -Al₂O₃ for CO₂ methanation showed that the larger particle size could promote the activity of the catalyst at a temperature lower than 458 K [107]. However, the activity of the catalyst could not be related to the particle size of the metal. The DRIFTS experiments showed that the CO was an active intermediate while the formate did not involve in the formation of methane. The doping of the additive can change the pathway of CO₂ methanation for noble metal-based catalysts. It has been reported that the doping of Ce on Ru/Al₂O₃ catalyst can significantly improve the activity and selectivity of the catalysts, 30% Ce modified catalyst possessing the best performance, which could be attributed to the formation of intermediates like formate and carbonate [112]. These species can then react with H₂ faster than with CO.

The addition of Mg onto Pd/SiO₂ catalyst could promote the formation of methane in CO₂ methanation reaction due to the stabilization of CO₂ on MgO [103]. Also, the CO acts then as an important intermediate in the reaction.

In conclusion, the Ru and Rh-based catalysts are most active for the noble metal catalysts in CO₂ methanation. The Ru and Rh catalysts are even active at a very low temperature near to ambient temperature with a very high CH₄ selectivity [156,166]. The CO acts as a main intermediate in the methanation process [156]. Although the excellent properties of Ru/Rh catalyst, their potential commercialization is limited due to their low availability and high cost.

Table 2.5 Summary of the noble-metal-based catalysts as compared to transition metal catalysts in CO₂ methanation.

Catalyst ^a	Metal	Preparation method ^b	Reaction condition			CO ₂	CH ₄	Ref.
	content (wt.%)		Temperature (°C)	H ₂ /CO ₂ ratio	GHSV/WH SV	conversion (%)	selectivi ty (%)	
Rh/MSN	5	WI	350	4	50,000 ml g _{cat} ⁻¹ •h ⁻¹	99.5	100	[109]
Ru/MSN						95.7	100	
Ir/MSN						9.5	83	
Ni/MSN						85.4	99.9	
Fe/MSN						4	92	
Cu/MSN						3.3	79	
Rh/TiO ₂	0.5	WI	350	4	90,000 ml g _{cat} ⁻¹ •h ⁻¹	72	99	[145]
Ru/TiO ₂						19	86	
Pd/TiO ₂						6	99	
Pt/TiO ₂						16	98	
Rh/SiO ₂	3	WI	350	5	60, 000 h ⁻¹	Ni=Rh>Pd	Rh>Ni> Pd	[71]
Pd/SiO ₂								
Ni/SiO ₂								
Rh/Al ₂ O ₃	3	WI	350	5	60, 000 h ⁻¹	Rh>Pd>Ni	Rh>Pd> Ni	
Pd/Al ₂ O ₃								
Ni/Al ₂ O ₃								
Rh/CeO ₂	3	WI	350	5	60, 000 h ⁻¹	Rh>Ni>Pd	Rh>Ni> Pd	
Pd/CeO ₂								
Ni/CeO ₂								

^a MSN: mesostructured silica nanoparticles; ^b WI-wet impregnation.

2.5.4.2 *Ni catalysts and other non-noble metal-based catalysts*

2.5.4.2.1. Ni-based catalysts

Ni-based catalysts were widely investigated in CO₂ methanation regarding their superiorities like good activity and CH₄ selectivity, low cost, high availability, and high accessibility making it appropriate in potential commercial applications [142,167]. A variety of Ni catalysts with good activity and selectivity e.g. Ni/CeO₂ [141], Ni/ZrO₂ [168], Ni/CeO₂-ZrO₂ [150], Ni/SBA-15 [169], and Ni/SBA-16 [142] have been developed for CO₂ methanation. Shohei et al. [170] synthesized the Ni/CeO₂ catalyst by wet impregnation method and compared its activity and selectivity with Ni/ α -Al₂O₃, Ni/TiO₂, and Ni/MgO. It was found that the Ni/CeO₂ catalyst showed the highest CO₂ conversion with CH₄ selectivity reaching nearly 1. Zhao et al. [168] prepared the Ni/ZrO₂ catalysts via combustion method using different combustion mediums and tested their activity in CO₂ methanation. It was shown that the combustion medium could significantly affect the physiochemical properties regarding Ni metal size, Ni dispersion, the crystal structure of the support, and Ni-support interaction of the catalyst, which significantly affected the activity and stability of the Ni/ZrO₂ catalyst. The CO₂ conversion of Ni/ZrO₂ synthesized by the urea medium reached 60% at 573 K under ambient pressure.

Although the superior performance of Ni-based catalysts, the problems of deactivation and poor stability still exist [171,172]. Thus, it is still a challenge to develop a highly stable Ni catalyst for CO₂ methanation [173]. At a low-temperature range lower than 573 K, the deactivation of Ni catalysts in CO₂ methanation was mostly caused by the sintering of Ni metal during the reaction process, which was caused by the formation of mobile nickel carbonyl originated from the interaction between Ni and CO [151,174–176]. At a high-temperature range of 623–723 K, the

coke may form owing to the Boudouard reaction and methane cracking. Apart from sintering of Ni metal and coke, the formation of Ni-hydroxide at low temperature was also found, which caused the decrease of the active phase of Ni [163]. Possible solutions toward tackling the problem were: (i) in adding promoter to improve the dispersion of Ni over the support or promote the formation of solid solution, (ii) in doping a metal to form an alloy, (iii) in modifying the support to obtain high surface area and pore volume, (iv) in making the catalyst with special structure, (v) in enhancing the metal-support interaction, and (vi) in changing the preparation method [173].

In the literature, it was also reported the addition of a second metal (Fe, Co, Cu) on Ni/ZrO₂ catalysts for CO₂ methanation [177]. Thus, the Fe-doped Ni/ZrO₂ catalyst significantly enhanced the activity of Ni/ZrO₂ catalyst at a low-temperature range when compared to the Co and Cu metals. The promotion of Fe could improve the dispersion and reducibility of Ni species and even promote the reduction of ZrO₂, which enhanced the adsorption and dissociation of CO₂ and H₂. Thus, the activity of Ni/ZrO₂ was improved. Moreover, the cerium had been reported to have positive effects on the mesoporous materials supported by Ni catalysts in CO₂ methanation [142,178].

Ewald et al. [172] studied the deactivation behavior of Ni-Al catalysts at 8 bar in CO₂ methanation. In the latter study, it was found that the Ni/ γ -Al₂O₃ catalyst synthesized by the impregnation method exhibited lower stability compared with the Ni-Al catalysts prepared by the co-precipitation method. The stability of the Ni-Al mixed oxides increased with the decrease of Ni content, but the activity of the mixed oxides showed a reversed trend. The deactivation mechanisms found over the Ni-Al catalysts were caused by the Ni metal sintering, a loss of specific surface area, a decrease of CO₂ adsorption capacity, decreasing medium basic sites, and structure change of the mixed oxide phase [172]. Moreover, the main deactivation reasons of impregnated catalysts were attributed to increased Ni particle size and decreased surface area. Also, the structure

and metal-support interaction could play predominant effects over some structure-sensitive catalysts in methanation. The special structure like hydrotalcite, phyllosilicate, and perovskite was reported to have good activity and stability towards CO₂ methanation [131,138,144,179,180]. By tuning the metal-support interaction, a stronger metal-support interaction can promote the Ni dispersion and thus promote the activity and stability of Ni catalysts in CO₂ methanation [181].

Ye et al. [173] synthesized a series of Ni/SiO₂ catalysts by different methods i.e. wet impregnation and ammonia evaporation method. The Ni/SiO₂ (AEM) catalyst prepared by the ammonia evaporation method exhibited Ni phyllosilicate with the lamellar structure, which enhanced the Ni-support interaction of the catalyst. It also had a high BET surface area, good dispersion of Ni, and small Ni particle size. The stability test for CO₂ methanation showed a higher yield of methane and better long-term stability than the impregnated Ni/SiO₂ catalyst. Liu et al. [171] prepared the Ni/SBA-15-op catalyst by one-pot hydrothermal method and compared its activity with the Ni/SBA-15-im synthesized by conventional wet impregnation method. It was revealed that the Ni/SBA-15-op catalyst showed higher surface area, larger pore volume, and higher Ni dispersion compared to Ni/SBA-15-im. Thus, both better activity and stability were obtained over Ni/SBA-15-op catalyst.

A) On the effect of the Ni loading and Ni dispersion

The performance of the Ni-based catalysts in CO₂ methanation depends on Ni metal size and Ni dispersion [167,182]. The nickel particle size can be affected by the Ni loading, the preparation method, and the support properties. Thus, the Ni particle size of the Ni/SiO₂ catalyst prepared by the deposition-precipitation method was affected by the parameters of the preparation method

[183]. The average Ni particle size of the catalyst derived from the Ni phyllosilicate phase was smaller than that of the Ni hydroxide derived catalyst. The Ni loading also has a significant effect on many Ni-based catalysts. Generally, the Ni particle size of the supported catalysts is smaller at low Ni loading and tends to increase for high Ni loadings [167]. For example, Ni nanoparticles supported over mesoporous SBA-16 reported in literature showed a decreasing trend towards Ni particle size as the increase of Ni loading [182]. In the same study, a catalyst with Ni loading of 5.9 wt.% showed the smallest Ni particle size and exhibited the highest turnover frequency (TOF) in CO₂ methanation reaction.

Herein, we have listed the effect of Ni loading on the Ni particle sizes of some supported catalysts and illustrated the influence of Ni particle size on the activity of the catalyst in methanation. As shown in Fig.2.11, the Ni particle size of Ni/MSN catalyst (mesostructured silica nanoparticle) increases with the increase of Ni loading, with the biggest particle obtained on the sample of 10 wt.% Ni loading [184]. The TOF and CO₂ conversion showed sharply increased trends with the increase of Ni loading until 5 wt.% of Ni and then only increased a little.

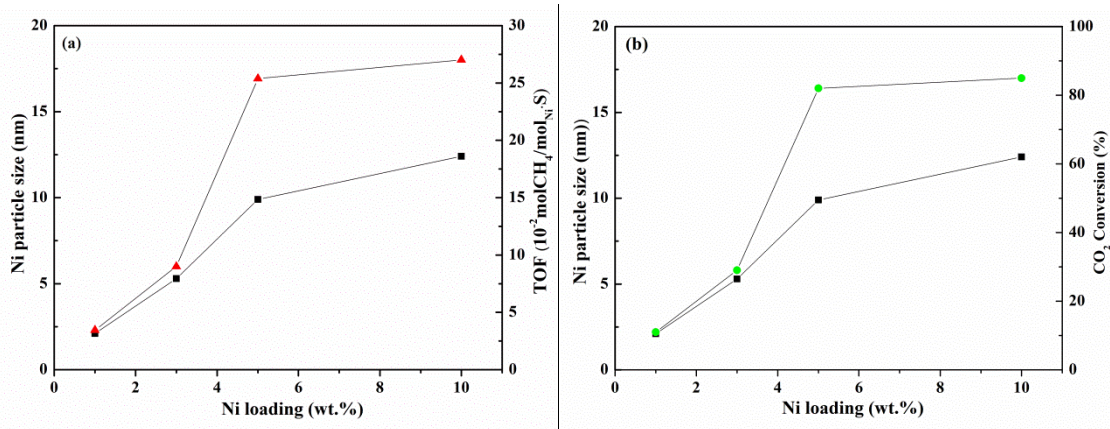


Figure. 2.11. Effect of Ni loading on the particle size and activity of Ni/MSN catalysts; Condition: GHSV = 50,000

$\text{mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$; $\text{H}_2/\text{CO}_2 = 4/1$; reaction temperature: 623 K [184].

A similar trend was also found on Ni/ γ -Al₂O₃ catalyst [185]. The increase of Ni loading resulted in the increase of Ni crystalline size from 10 to 25 wt.%, with the highest CO₂ conversion obtained over 20Ni/ γ -Al₂O₃ at 573 K. Generally, the increase of Ni loading can promote the activity of the catalyst due to more active metals for the reactant, but a high Ni loading may result in the aggregation of Ni species and decrease of Ni dispersion, which leads to the decrease of activity. Nevertheless, the effect of Ni content on the Ni crystalline size depends on the type of support. The increase of Ni content in hydrotalcite derived catalysts can lead to the decrease of Ni crystalline size for the reduced and spent catalysts [131]. In the CO₂ methanation reaction, the activity of the catalyst increased as an increase of Ni content until 42.5 wt.% at the temperature range of 523-923 K.

The preparation method also plays an important role in the dispersion of Ni catalysts. The Ni/Al₂O₃ catalysts prepared by the co-precipitation method showed a higher Ni dispersion compared to the one prepared by the impregnation method due to the formation of surface NiAl₂O₄ spinel phase [186].

B) On the Influence of the support on the performance of Ni-based catalysts

The support itself has a significant effect on the performance and stability of catalysts. The dispersion of Ni, the basicity, the metal-support interaction, and the morphology of the catalyst can be affected by the used support [160,167,187]. The support with high surface area and pore volume can confine the Ni particles inside the porous structure and thus improve the dispersion of Ni [142]. The mesoporous support like SBA-15, SBA-16, or KIT-6 with high surface area and

pore volume had been reported to promote the dispersion of Ni and lead to small Ni particles [60,179,188–190].

The basicity of supported catalyst plays an important role because the support can also participate in the reaction due to its CO₂ adsorption/desorption capacity. It has been reported that the Ni/Ce_{0.5}Zr_{0.5}O₂ catalyst exhibited more medium basic sites compared to that of Ni/ γ -Al₂O₃ catalyst. This medium basicity promoted the formation of monodentate carbonate, thus resulting in the formation of monodentate formate species, which was hydrogenated to methane with a higher rate [160]. Also, Ni/ γ -Al₂O₃ catalysts showed lower performance than the Ni/Ce_{0.5}Zr_{0.5}O₂ catalysts due to the lack of medium basic sites. CeO₂ supported nickel catalysts were intensively studied in CO₂ methanation because of their superior performance and selectivity toward CH₄, which could be attributed to the unique redox properties of cerium oxide [191]. The cerium oxide can be reduced partially to form defective sites on the support, which resulted in the formation of oxygen vacancies, which will promote CO₂ adsorption and dissociation [192].

The metal-support interaction is also controlling Ni particle size and oxygen availability of Ni-based catalysts. The small particle size could be favored under strong metal-support interaction [193,194]. Lin et al. [195] investigated the effect of activation treatment on the metal-support interactions (MSI) of Ni/CeO₂ catalysts. It was found that the Ni/CeO₂ catalyst pre-treated under H₂ atmosphere showed better activity and high selectivity compared to catalysts pre-treated under N₂ or air atmosphere, which was attributed to the appropriate MSI generated in the pre-treatment, leading to the high dispersion of Ni, high amount of oxygen vacancies, and abundant weak basic sites on the catalyst [195]. Regarding regulating the MSI of the catalyst, the preparation method also plays a key role. Yan et al. [187] reported the Ni/Y₂O₃ catalyst prepared by impregnating Ni onto different Y precursors like Y₂O₃, Y₄O(OH)₉(NO₃), and YO(NO₃) for CO₂ methanation. The

MSI of the catalyst was changed because of different Y precursors, in which the YO(NO₃) material supported Ni catalyst showed the moderate metal-support interaction between Ni and Y₂O₃, leading to superior activity for CO₂ methanation and good stability in CO-containing reactants [187]. In conclusion, a moderate metal-support interaction can thus improve the dispersion of Ni, and increase basicity and oxygen vacancies of Ni catalysts, leading then to a better activity and stability in CO₂ methanation.

The morphology of Ni-based catalysts also contributes to the activity and stability of catalysts in CO₂ methanation. Bian et al. [196] prepared the Ni/CeO₂ catalyst with different CeO₂ morphologies and carried it out in low-temperature CO₂ methanation. The Ni/CeO₂ (NR) catalyst with nanorod structure exhibited superior performance than Ni/CeO₂ (NC) catalyst with nanocube structure. This high activity was attributed to the higher Ce³⁺ ratio on the surface of the catalyst. Zhou et al. [192] synthesized the CeO₂ materials by hard-template, soft-template, and precipitation method and used them to prepare Ni/CeO₂ catalysts. It was shown that the hard-template method prepared sample (NCT) showed a well-developed mesoporous structure with the highest SSA. Meanwhile, the soft-template prepared sample (NCS) displayed a disordered structure with a smaller pore diameter. The precipitation method prepared sample (NCP) only showed the nanoparticles with disordered structure. The NCT catalyst performed the highest CO₂ conversion among the studied catalysts in methanation reaction. NCP catalyst showed then lower activity, which could be attributed to the low surface area and poor porosity.

The most intensively used support such as CeO₂ [158,191,196], ZrO₂ [197], SiO₂ [197], Al₂O₃ [198], MgO [191,199], Y₂O₃ [187,198], Ce_{0.5}Zr_{0.5}O₂ [200], TiO₂ [147], carbon nanotube [201], zeolite [202], clays [203], SBA-15 [171], SBA-16 [142,204], and hydrotalcite [131,138,144,205–208] were widely reported in the literature. Other transition metal oxide supports such as : Sm₂O₃

[198], ZrO₂ [168], CeO₂ [192], Ce_xZr_{1-x}O₂ [209], Y₂O₃[210], have shown superior activity and stability when compared to Al₂O₃ based-catalyst. However, these supports contain VIII group metals which are not abundant and have high cost.

Table 2.6 summarizes the main supports that have been studied intensively in CO₂ methanation. As shown in the table, Ni catalysts supported on different support showed very different performance in CO₂ methanation. As the difference of physicochemical properties for various supports, the physicochemical parameters of Ni catalysts were also deeply changed by the support. Therefore, the activity and selectivity of the catalysts were significantly affected.

Hiroki et al. [198] synthesized the Ni catalysts supported on various supports by conventional incipient wet impregnation method and investigated their performance in CO₂ methanation. The CO₂ conversion comparison at 548 K under atmospheric pressure was displayed in Fig.2.12. The Y₂O₃ supported Ni catalyst showed the highest CO₂ conversion compared to other metal oxide supported Ni catalysts, which could be partly attributed to the effects of basicity and surface intermediates during the reaction that presented on the materials [198]. By FTIR technology, the Ni/Al₂O₃ catalyst proceeded by a CO methanation process. Only carbonates were found on Ni/La₂O₃ catalyst. Meanwhile, the formate species from the carbonates were detected on Ni/Y₂O₃ catalyst.

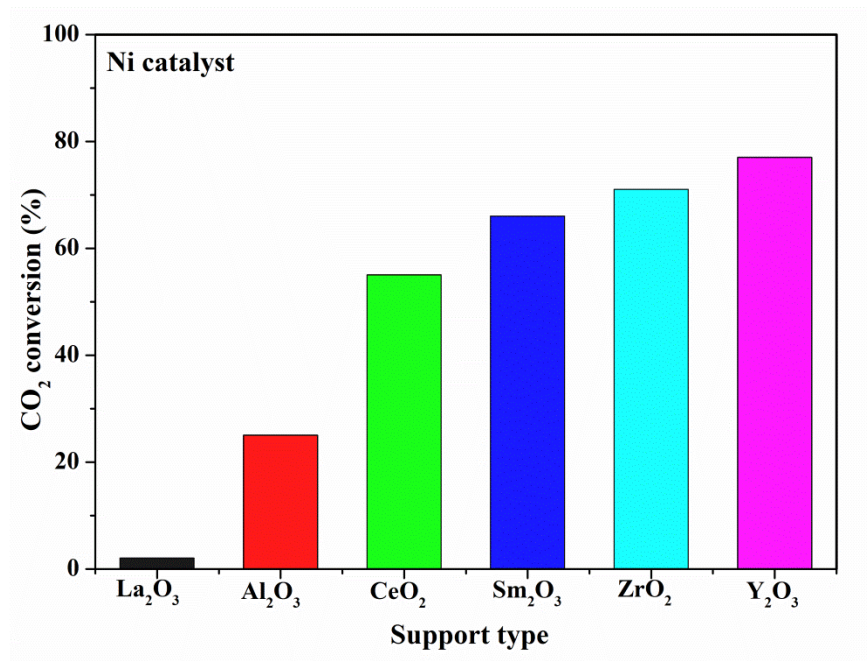


Figure. 2.12. Comparison of CO₂ conversion for Ni catalysts supported on different metal oxides; Condition: 548 K, atmospheric pressure, WHSV= 20,000 kg⁻¹h⁻¹.

The CeO₂ supported Ni catalysts reported in other literature exhibits superior activity and stability due to their effects of morphology and oxygen mobility property [196]. Furthermore, the ZrO₂ and Ce_{0.5}Zr_{0.5}O₂ also showed good activity because they also had oxygen storage capability. Jia et al. [136] prepared the Ni/ZrO₂ catalyst by plasma decomposition of Ni precursor and compared its activity to that of Ni Ni/ZrO₂ catalyst obtained by a conventional thermal decomposition. It was revealed that the plasma decomposition derived catalyst higher Ni dispersion, high concentration of Ni(111) plane, and stronger coordination between Ni and interfacial sites, leading to a fast H₂ dissociation and more oxygen vacancies, thus a higher activity was obtained compared to the thermally processed catalyst. Also, the mechanism in methanation was different regarding different catalysts; the plasma processed catalyst experienced a carbon oxide hydrogenation route while the thermally processed catalyst had a formate hydrogenation pathway. Regarding

Ni/Ce_xZr_yO₂ catalyst, it also proceeds through the formate species originated from carbonate hydrogenation with the CO species as a by-product [211].

Ordered mesoporous silica such as SBA-15/16 can also be potential thanks to their high surface area and confinement of porous structure, making it possible to obtain small nanoparticles of Ni. The Ni nanoparticles over Ni/SBA-16 catalyst can reach 4.3 nm with a high surface area [142]. With the incorporation of Ce, good activity and stability can be obtained over the Ni/Ce/SBA-16 catalyst.

The hydrotalcite-derived mixed oxides catalysts also attracted attention because they not only generate small particles of active metals but also maintain high stability in the high-temperature range. For instance, the low loading of yttrium doped hydrotalcite derived Ni catalyst reached a CO₂ conversion of 81% at 523 K under atmosphere pressure [144]. Its higher performance was attributed to the strong metal-support interaction, the high ratio of medium basic sites, and the small Ni particle size.

Other novel materials were also applied as Ni-based catalysts for methanation. Thus, metal-organic framework (MOF) materials were used as support to prepare catalysts due to their high surface area of more than 1,000 m²•g⁻¹. Lin et al. [212] synthesized the Ni@C (designated name by author) catalyst from MOF-derived hierarchical hollow spheres and used it in CO₂ methanation. The as-prepared catalyst possessed a high surface area and rich isolated active sites. The methanation test showed that the catalyst achieved a CO₂ conversion of 100% and CH₄ selectivity of 99.9% at 598 K under atmospheric pressure and it also exhibited good stability at 523 K.

In conclusion, the activity, selectivity, and stability of the Ni catalysts deeply depended on the properties of the support. Thus, the basicity, porosity, and redox property of the support can

substantially influence the methanation reaction. For example, over hydrotalcite-derived Ni catalysts, a linear correlation was found between the basicity of the catalysts and CO₂ activity in methanation [131].

Table 2.6 Catalytic performance of the Ni catalysts supported on different materials for CO₂ methanation.

Material	Ni content (wt.%)	Preparation method [*]	Reaction condition			CO ₂ conversion (%)	CH ₄ selectivity (%)	Ref.
			Temperature (°C)	H ₂ /CO ₂ ratio	GHSV/ WHSV			
γ -Al ₂ O ₃	10	WI	300	4	5700 h ⁻¹	82	99	[213]
Mesoporous γ -Al ₂ O ₃	15	WI	300	3.5	9000 mL/g _{cat} ·h	46	99	[185]
Mesoporous γ -Al ₂ O ₃	20	WI	300	3.5	9000 mL/g _{cat} ·h	73	99	[185]
Mesoporous γ -Al ₂ O ₃	25	WI	300	3.5	9000 mL/g _{cat} ·h	63	98	[185]
No support	100	WI	400	5	52,300 h ⁻¹	44	58	[214]
Al ₂ O ₃	125	WI	400	5	52,300 h ⁻¹	42	81	[214]
Al ₂ O ₃	16	WI	500	5	52,300 h ⁻¹	75	100	[214]
Al ₂ O ₃	39	WI	500	5	52,300 h ⁻¹	81	93	[214]
MgO	5.8	sonochemical	400	8	47,760 h ⁻¹	85	98	[215]
MgO	5.8	co-precipitation	400	8	47,760 h ⁻¹	63	-	[215]

MgO	5.8	solution combustion	400	8	47,760 h ⁻¹	71	-	[215]
TiO ₂	10	WI	350	4	60,000 h ⁻¹	42	74	[216]
TiO ₂	10	DBD-plasma	350	4	60,000 h ⁻¹	60	98	[216]
TiO ₂	6.17	DBD-plasma- rinse	350	4	60,000 h ⁻¹	72	99	[216]
SiO ₂	5	WI	350	4	60,000 mL/g _{cat} ·h	48	94	[217]
SiO ₂	10	WI	350	4	60,000 mL/g _{cat} ·h	53	95	[217]
SiO ₂	15	WI	350	4	60,000 mL/g _{cat} ·h	54	95	[217]
La ₂ O ₃	50	CSCM	400	4	120,000 mL/g _{cat} ·h	60	88	[218]
ZrO ₂	10	WI	350	4	60,000 mL/g _{cat} ·h	66	97	[136]
ZrO ₂	8.68	DBD-plasma	350	4	60,000 mL/g _{cat} ·h	77	99	[136]
CeO ₂	10	WI-CP	340	4	45,000 mL/g _{cat} ·h	67	100	[192]
CeO ₂	10	WI-HTM	340	4	45,000 mL/g _{cat} ·h	90	100	[192]
Ce-Zr	10	WI	300	4	20,000 mL/g _{cat} ·h	48	99	[219]
SBA-15	15	OP	420	4	10,000 mL/g _{cat} ·h	75	99	[171]
SBA-15	15	WI	420	4	10,000 mL/g _{cat} ·h	68	99	[171]
MCM-41	20	precipitation	420	4	9,000 mL/g _{cat} ·h	72	98	[220]
SBA-16	10	WI	400	4	12,000 h ⁻¹	73	98	[142]
USY	15	WI	400	4	43000 mL/g _{cat} ·h	68	93	[221]

hydrotalcite	20	precipitation	300	4	12,000 h ⁻¹	87	99	[144]
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*WI-wet impregnation; DBD-plasma-rinse: rinse after dielectric barrier discharge (DBD) plasma decomposition; CSCM: colloidal solution combustion method; WI-CP: Support prepared by precipitation method with the catalyst prepared by wet impregnation; WI-HTM: HTM-KIT-6 hard template method for support, wet impregnation for catalyst; OP: one-pot hydrothermal method

C) On the effect of the promotion on the performance of Ni-based catalysts in methanation reaction

It is well reported that Ni catalysts without additives suffered from low CH₄ selectivity, poor stability, and deactivation problems due to the metal sintering at high temperatures [222]. Thus, promoter elements such as: Mg [179], La [169,208,223], Ce [142,224,225], Zr [226], Y [141,227], Co [228,229], Fe [203,229] and Cu [215,229] etc. had been applied to improve the performance of Ni catalysts. The Ni/Al₂O₃, as a commonly studied catalyst in CO₂ methanation due to its economic advantage, was doped by CeO₂, La₂O₃, Sm₂O₃, Y₂O₃, and ZrO₂. The catalytic performance of the synthesized catalysts was investigated by a series of technologies [230]. It was found that the addition of these promoters had a positive effect on the performance of the Ni/Al₂O₃ catalyst, and the La-promoted catalyst showing the best activity and stability. At 573 K, the CO₂ conversion decreased as the following sequence: NiLa>NiCe>NiSm>NiY>NiZr>Ni/Al₂O₃. The authors attributed these results to the improvement of nickel reducibility, nickel dispersion, and the presence of moderate basic sites. The La additive is a very promising promoter for Ni/γ-Al₂O₃ catalysts in CO₂ methanation. Furthermore, the effect of La content on the performance of Ni/La-γ-Al₂O₃ catalysts for CO₂ methanation was also studied, in which the 14 wt.% La-doped Ni/La-γ-Al₂O₃ catalyst showed the best performance with nearly 100% of CH₄ selectivity at low

temperature [231]. This latter result was assigned to the enhanced basicity of La- γ -Al₂O₃ support and the reducibility of NiO. The presence of La also showed a good improvement in CO₂ methanation for the Ni/SBA-15 catalyst, which was also a widely investigated catalytic system [169]. The perovskite structure of LaNiO₃ was formed on Ni-La₂O₃/SBA-15(C) catalyst prepared by citrate complex method, leading to the enhanced interaction between La₂O₃ and Ni. Thus, high dispersion of Ni and small Ni particles (less than 5 nm) were obtained. In CO₂ methanation, the Ni-La₂O₃/SBA-15(C) catalyst showed a high CO₂ conversion of 90.7% and CH₄ selectivity of 99.5% at 593 K [169]. The La-modified mesostructured cellular foam (MCF) supported Ni catalyst with phyllosilicate structure also showed a good performance in CO₂ methanation as reported in a new study [223]. This is attributed to the small Ni particle size, high capacity of H₂ and CO₂ adsorption, and low activation energy.

In Table 2.7, the Ni catalysts supported on different materials doped by various promoters for CO₂ methanation were summarized. As shown in Table 2.7, the adding of the promoter can cause a significant effect on the physicochemical properties of the Ni catalysts. The parameters like dispersion of Ni, the reducibility of Ni, the basicity of catalyst, metal-support interaction, oxygen vacancies, anti-sintering of Ni particles, etc. have been changed by the promoters. Thus, the activity, selectivity, and stability of catalysts were affected significantly.

Table 2.7 Ni catalysts promoted by different additives reported in the literature.

Catalyst	Promoter	Loading (wt.%)	Ni (wt.%)	Effect of promoter addition	Ref.
NiUSY	Ce	15	5	A large number of carbonates, promoting CO ₂ conversion to CO.	[225]
Ni/SBA-16		10	10	Increased Ce ³⁺ ratio and oxygen vacancies, enhanced moderate basicity	[142]

Ni/ γ -Al ₂ O ₃		15	15	Increased metal-support interaction, medium basic sites, and adsorbed CO ₂ . More Ni metal species and oxygen defects on the surface	[232]
Ni/MCM-41	Zr	$n_{Zr}/n_{Si}=0.0$ 1, 0.03, 0.1, 0.15	10	Strengthened Ni-Zr interaction which favored the spillover of H, increased surface oxygen species. 0.01 is the best Zr content, which showed the best performance	[233]
Ni/CeO ₂	Y	2	5	The decreased particle size of CeO ₂ , increased specific surface area and the number of oxygen vacancies, enhanced metal-support interaction, promoted the formation of CeO ₂ nanorods.	[141]
Ni/SBA-15	Mg	5	10	Increased medium basic sites and promoted the formation of monodentate formate.	[179]
Ni/Al@Al ₂ O ₃	K	0.5	10	Decreased activity was attributed to decreased amount of Ni active sites and basic sites.	[234]
Ni-Al ordered mesoporous composite	Ca	$N_{Ca}/n_{Al}=1$, 3,5,8,10	$n_{Ni}/n_{Al}=10$	Enhanced surface basicity and decreased active energy.	[235]
Ni/SiO ₂	La	10	10	Better dispersion of Ni and a higher proportion of moderate strength basic sites.	[236]
Ni/SiO ₂	Cu	1	10	Increased CO selectivity indicates favoring the RWGS reaction. Slightly increased the resistance of metal sintering	[217]
Ni/Zr-clay	Co	1	15	Promoted the dispersion of NiO nanoparticles, increased quantity of the reduced active nickel species.	[203]
Ni-MgO		2	4.3	Decreased active energy, more active sites.	[215]
Ni/Zr-clay	Fe	1	15	Increased dispersion of Ni, increased Ni reducibility	[203]
Ni/(Mg, Al)O _x hydrotalcite		1.2-18	12	Increased Ni nanoparticle size, decreased Ni dispersion, enhanced CO dissociation, and basicity.	[237]
Ni-Al		10	44	The formation of a Ni-Fe alloy increased the thermal stability of catalysts.	[238]
Ni-Al	Mn	10	44	A higher density of medium basic sites and an enhanced CO ₂ adsorption capacity.	[238]
Ni/bentonite	V	3,5,8	20	Enhanced H ₂ uptake and Ni dispersion, promoted the dissociation ability of CO.	[239]

Besides the aforementioned catalytic systems, Lanthanum was also used to improve the activity of hydrotalcite-derived Ni catalysts (HTN) in CO₂ methanation [206,208]. It was found that the 2 wt.% of La-doped HTN catalyst showed the highest CO₂ conversion at low temperature, which could be attributed to the increase of basicity caused by La incorporation. The different methods of promoter incorporation also have a significant effect on the performance of the La-doped HTN catalyst. The catalyst prepared by the ion-exchange method showed both the higher CO₂ conversion and CH₄ selectivity at low temperature (573 K) as well as superior stability. This remarkable activity was attributed to the increase of medium basic sites and the presence of smaller Ni crystal size [206].

Ceria (cerium oxide) is also known to be an important additive for Ni-based catalysts in various CO₂ utilization reactions [142,232]. As for Ni/Al₂O₃ catalyst, it has been reported that the adding of Ce on Ni/Al₂O₃ catalyst can significantly promote the activity and CH₄ selectivity in methanation. The optimum promotion was found with 15 wt.% of CeO₂. This catalyst showed the best CO₂ conversion and high CH₄ selectivity at the temperature range from 523 to 673 K. In such catalysts, the presence of ceria promoted the higher dispersion of Ni, the smaller Ni particle size, the higher amount of medium basic sites, the higher oxygen deficiencies, and finally the higher surface ratio of Ni⁰ and Ce³⁺, all which contribute to a better activity and stability of the catalyst. Also, in such catalyst, the Ce⁴⁺ cation can be reduced to Ce³⁺ state under the pre-treatment of hydrogen, leading to the formation of oxygen vacancies, which can then lead to a promotion of the adsorption and dissociation of CO₂ species [141]. Due to the unique redox and oxygen deficiency properties, the ceria is widely used as a promoter in the preparation of Ni catalysts.

In the literature, the Ce doped Ni/SBA-16 catalysts were prepared and their catalytic performance was evaluated in CO₂ methanation [142]. The results indicated that the presence of Ce led to the formation of oxygen vacancies, which could significantly promote the CH₄ selectivity. The

mesoporous SBA-16 can disperse the Ni and Ce species well and confine the Ni and Ce particles inside the mesoporous channels. The highest ratio of Ce³⁺, highest amount of medium basic sites, and good dispersion of Ce have been obtained over 10 wt.% Ce-doped Ni/SBA-16 catalyst, leading to the best activity and high CH₄ selectivity.

Zirconia or zirconium oxide also can act as the oxygen storage material and has been intensively studied in many CO₂ utilization reactions [226,233]. Yang et al. [233] studied the effect of Zr on MCM-41 supported Ni catalyst for CO₂ methanation. It was found that the adding of Zr strengthened interaction between Ni and Zr, leading to the spillover of H species adsorbed on the surface of Ni to the support, which is favorable for the hydrogenation of CO₂-derived intermediates [233]. Also, the addition of Zr promoted the increase of oxygen species at the surface, and the decrease of strong basicity, which contribute to hinder the carbon deposition and the removal of deposited coke under reaction. However, an excess Zr on the support would be harmful to the activity of the catalyst due to the destruction of the ordered structure of the support.

The alkaline earth like Mg can also be a good additive alternative for Ni catalyst [179,240]. Plaifa et al. [179] Ni-Mg phyllosilicate mesoporous SBA-15 catalysts with different Mg loading by ammonia evaporation method and applied them in CO₂ methanation reaction. It was found that the presence of Mg of 5 wt.% onto Ni/SBA-15 catalyst could improve the increase of medium basic sites, which enhanced the methanation activity at low temperature. Also, the phyllosilicate structure could enhance the metal-support interaction, which suppressed the metal sintering, leading to good stability of the catalysts. The other alkaline earth metal oxides like Ca, Sr, and Ba were also studied for Ni catalysts [240]. The incorporation of alkaline earth on Ni/CeO₂ catalysts can promote the dispersion of Ni, an increase of moderate basic sites, and more oxygen deficiencies of the catalyst, thus improve the activity of the catalysts. The activity test showed that

the Ca doped Ni/CeO₂ catalyst performed the best activity due to the highest Ni dispersion and largest moderate basicity. Besides the promotion of individual additives, the addition of two additives like Ce-Zr is also widely studied for Ni catalyst, which shows good modification [241]. Thus, the addition of Ce-Zr solid solution on activated carbon (AC) supported Ni catalyst can result in stronger interaction between Ni and Ce-Zr, higher dispersion of Ni, and high CO₂ adsorption ability, leading to high CO₂ conversion and CH₄ selectivity [241]. Li et al. [242] studied the effect of ceria promotion on the performance of Ni-La/ZrO₂ catalyst in CO₂ methanation. The results revealed that the Ni-Ce-La/ZrO₂ catalyst showed better activity and high stability than the Ce or La modified Ni/ZrO₂ and the non-modified Ni/ZrO₂ catalyst. The adding of Ce on Ni-La/ZrO₂ catalyst could promote the activation of CO₂ and the Ni nanoparticles of Ni-Ce-La/ZrO₂ catalyst had a high resistance to metal sintering.

The additives with more than two metal oxides also had attracted intensive attention. The Ni catalysts supported on γ -Al₂O₃ based on composite oxide were employed in CO₂ methanation [243]. The γ -Al₂O₃-ZrO₂-TiO₂-CeO₂ (equivalent loading for the additive, 15%) composite oxide supported Ni catalyst possessed higher Ni dispersion and better reducibility, leading to higher activity compared to that of Ni/ γ -Al₂O₃ catalyst.

2.5.4.2.2. Other non-noble metal-based catalysts for CO₂ methanation

Besides Ni catalyst, Iron (Fe) [121] and cobalt (Co) [29,244–246] catalysts were also studied in CO₂ methanation. Zeynep et al. [121] studied Fe catalyst promoted by different additives in CO₂ methanation. It was found that the bare Fe catalysts showed very poor activity and CH₄ selectivity and the Fe catalysts doped by promoters did not perform a comparable activity and CH₄ selectivity as a comparison to Ni-based catalyst. Among the promoters, the Mg of 2 wt.% modified Fe catalyst

exhibited the best positive effect. At a harsh condition (8 bar), the highest CH₄ yield reached 32% at 673 K for 2Mg/Fe₂O₃ sample.

Co-based catalysts can exhibit comparable activity in comparison to Ni ones in CO₂ methanation. Liang et al. [123] investigated alumina-supported Ni and Co catalysts in CO₂ methanation. It was found that the Co/Al₂O₃ catalyst showed higher activity than that of Ni/Al₂O₃. This is attributed to the better coordination effect between Co and alumina when compared to Ni on Al₂O₃. This coordination effect can promote the hydrogenation of intermediates such as bicarbonate, formate, and carbonate species. The CO₂ can be activated on the surface of Co metal and subsequently mitigate and react with the hydroxyl in the alumina to form the intermediates. Such intermediates can be hydrogenated to methane over cobalt sites. Also, ZrO₂ supported cobalt catalysts were also employed to catalyze the CO₂ methanation reaction. It was reported that the Co/ZrO₂ catalysts prepared by the organic acid-assisted impregnation method could exhibit superior activity compared to the catalyst prepared without organic acid [127]. Within these organic acids, carboxylic acids with a longer chain containing more carboxyl and hydroxyl groups showed good improvement for the catalytic performance of Co/ZrO₂ catalysts as compared to the conventional method prepared catalyst. Meanwhile, the amino acid could change the charge properties of the surface of ZrO₂ by changing the pH and increase the Co dispersion, thus exhibited better performance than the conventional one. In all the organic acids, the Co/ZrO₂ catalysts derived from the citric acid-assisted impregnation exhibited the best activity and the highest TOF value with a CO₂ conversion of 85% and a CH₄ selectivity of 99% as well as TOF of 1116 h⁻¹ at 673 K and 30 bars. This high activity was attributed to the improved Co dispersion and enhanced Co-ZrO₂ interaction, resulting in more oxygen vacancies and high CO₂ adsorption capacity. The Co-based

catalysts prepared by the liquid reduction method can even reach high activity that is comparable to the noble metal-based catalysts at low temperature (<473 K) recently in the literature [126].

Apart from being a catalyst itself, cobalt can also play an important role as a promoter in improving the performance of the Ni-based catalysts. Liu et al. [228] reported that the addition of Co could improve the activity of ordered mesoporous Ni-Co/Al₂O₃ catalyst, which was attributed to the enhanced H₂ sorption capacity. Also, the ordered mesoporous structure contributed to achieving high stability. In conclusion, the Co-based catalysts can exhibit good performance in CO₂ methanation. However, Ni-based ones remained the most promising.

2.5.6 Power-to-gas system (PtG)

The flow chart of the PtG project was shown in Fig.2.13. The electricity from the renewable energy power plant or conventional power plant was used to electrolyze water to produce H₂. The captured CO₂ reacted with H₂ to produce CH₄. Then, CH₄ was transported and used as fuel or raw material. The PtG process can act as an important energy storage route. Compared to existing storage ways, the PtG route has a longer discharge time as shown in Fig.2.14.

The main energy consumption parts of the PtG route are the electrolysis part and the methanation part. For the electrolysis, it can be improved by applying a new electrolytic method like the solid oxides method. The methanation process can be promoted by controlling the reaction parameters and applying high-performance catalysts.

The development of novel CO₂ methanation catalysts is then the main topic of this thesis.

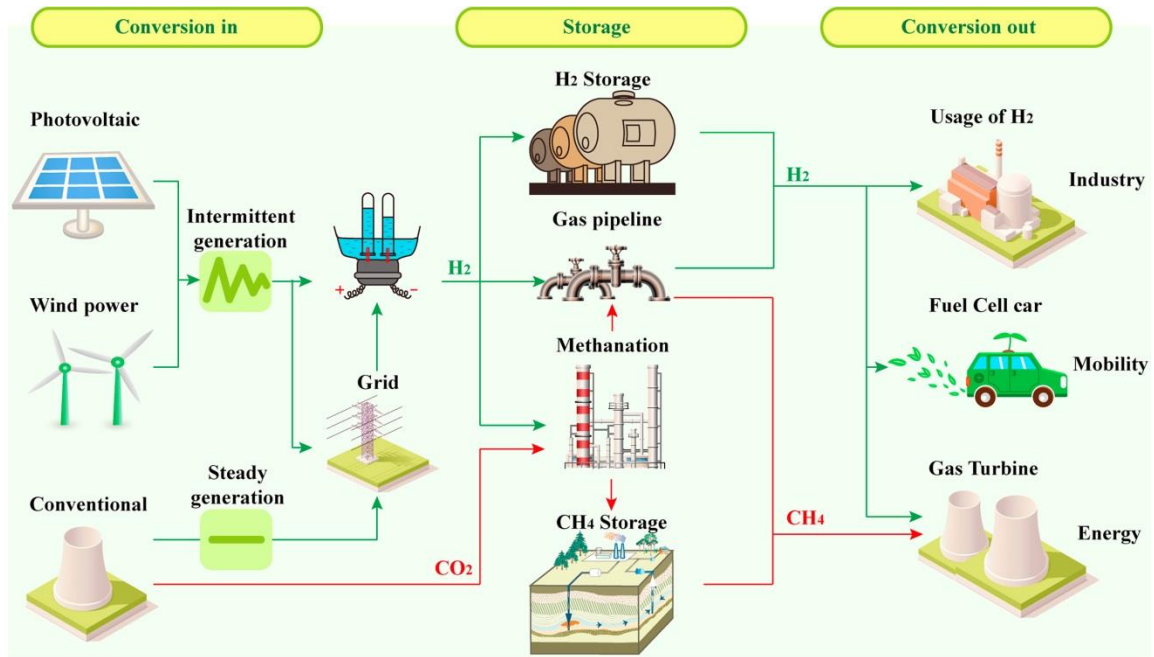


Figure 2.13. PtG technology flow chart; Adapted from [247]

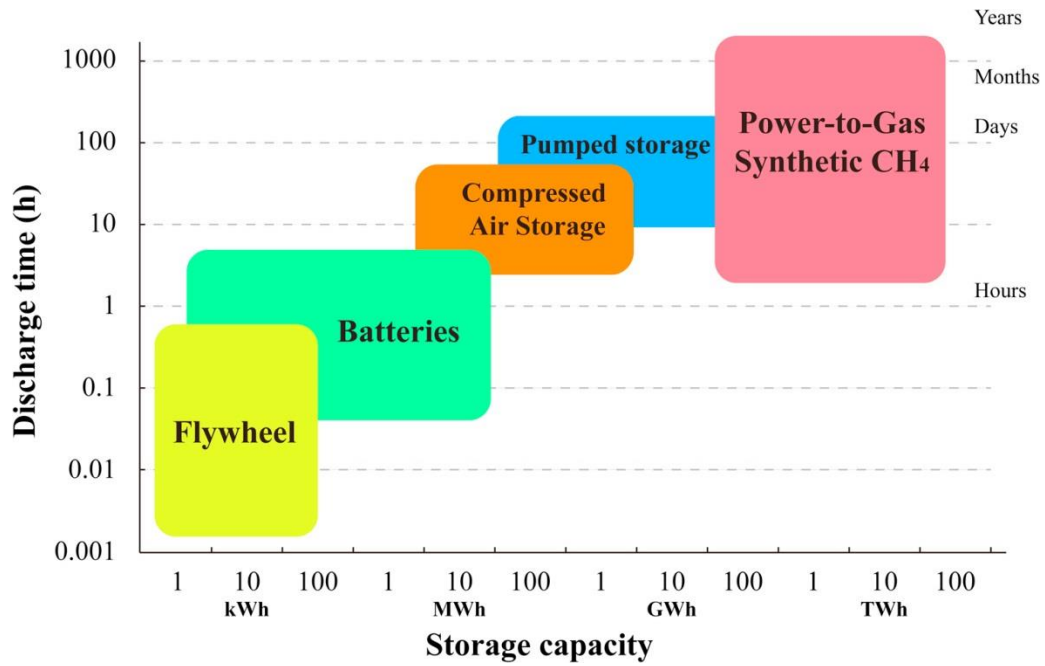


Figure 2.14. Storage routes for excess energy with the relationship between discharge time and storage capacity.

Adapted from [247].

2.5.6.1. The PtG projects in European Union

Table 2.8 lists some PtG projects in Europe, which use chemical/biological conversion systems.

The European Union (EU) has the most PtG plants in the world now.

Table 2.8 Power-to-Methane plants in European Union. Adapted and modified from [248]

Installation	Methanation principle	Power [kW]	*Electrolysis	Status (Spring 2021)
Etogas - Audi AG	Chemical	6300	Alkaline	Operational
Solothurn (Store&Go project)	Biological	700	PEM	Planned
Niederaussem	Chemical	300	PEM	Finished
Foulum - Electrochaea	Biological	250	PEM	Finished
Alzey - Exytron (Exytron GmbH)	Unknown	63	Alkaline	Planned
Rostock – Exytron Demonstrations	Unknown	twenty one	Unkown	Operational
Stralsund (University of Applied Sciences Stralsund)	Unknown	20	Alkaline	Planned
Rozenburg	Chemical	10	PEM	Operational

*PEM – Polymer electrolyte membrane electrolysis.

2.5.6.2. Non- European Union: The example of China

As shown in Fig.2.15, the top 6 countries which have the highest renewable energy power generation capacities in the world were displayed. It can be seen that China has the biggest renewable energy power generation capacities. Although the biggest share of renewable energy, there are relatively few PtG (CH₄) demonstration plants in China. Until now, there is only one PtG (H₂) plant located in the province of Hebei, which uses surplus wind energy to produce hydrogen.

Even in EU, the most plants are located in Germany. However, given the ecological and economic benefits of the PtG route, there are plenty of potentials of such route in the storage of renewable energy. For example, wind and solar energy abandonment have been serious in China, which PtG technology can help to alleviate this situation. Moreover, if the carbon tax is considered in the future, policy factors and economic factors will be very beneficial to the development of PtG [247]. With the rapid development of renewable energy, the PtG process will be necessary to solve the storage problem.

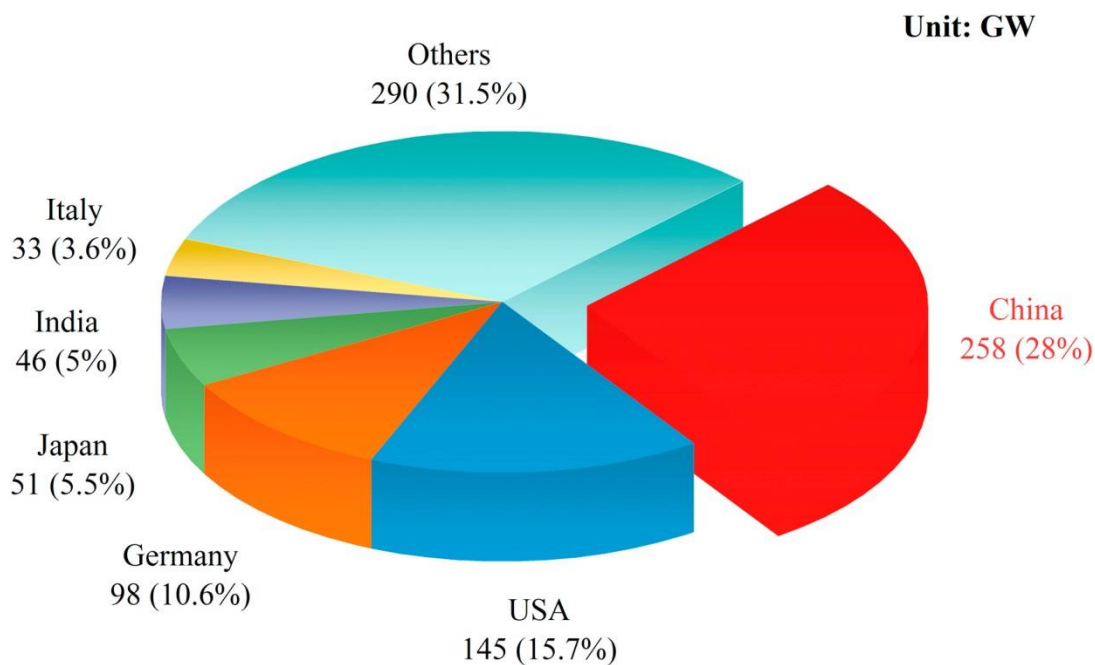


Figure 2.15. Renewable energy power generation capacities distribution in the world in 2016; adapted from [247]



Chapter III

Experimental part

3. Experimental part

3.1 Catalyst preparation

In this thesis, different catalysts were prepared by different synthesis strategies as shown in Fig.3.1.

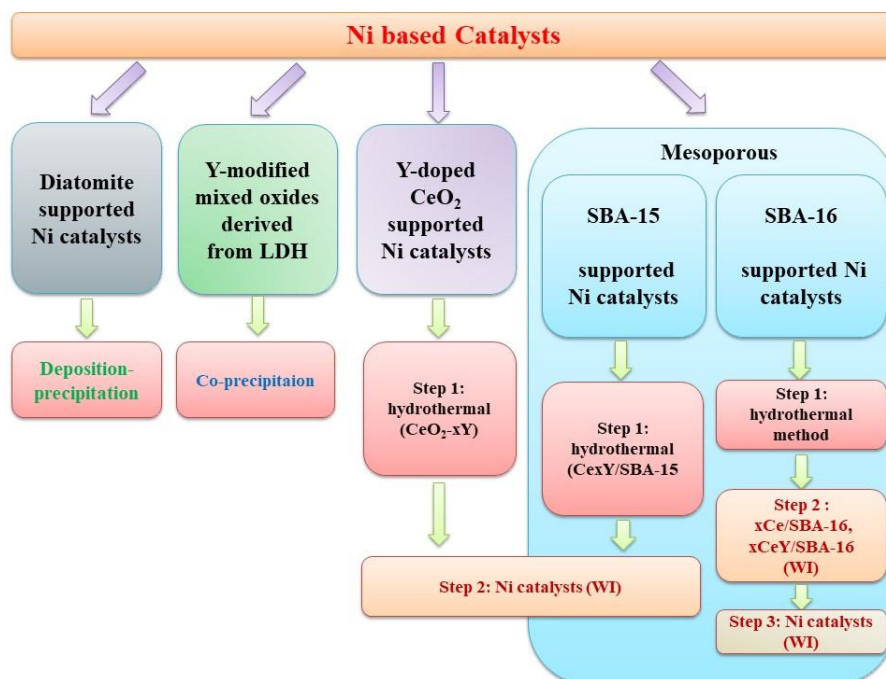


Figure 3.1. Syntheses strategies of the Ni catalysts in the thesis.

Thus, depending on the synthesized catalyst we used deposition-precipitation, co-precipitation, hydrothermal synthesis, wet impregnation, etc.

3.1.1 Low-cost diatomite supported catalysts

This work was carried out during collaboration with the University of Belgrade. The preparation of support and catalysts was thus carried out in Serbia [249]. Crude diatomite material was supplied from Prilep (The Republic of North Macedonia). The crude material was mechanically, chemically,

and thermally treated to obtain the desired support properties. The supported Ni-Mg catalysts were prepared using the precipitation-deposition (PD) method.

Precipitation of Ni and Mg species was performed by addition of anhydrous Na_2CO_3 to a salt solution containing $\text{Ni}(\text{SO}_3\text{NH}_2)_2$, $\text{Ni}(\text{NO}_3)_2$, or $\text{Ni}(\text{CH}_3\text{COO})_2$, and $\text{Mg}(\text{NO}_3)_2$ in a molar ratio of Ni/Mg=10. The resulting suspension was vigorously stirred and heated up to 90°C . The deposition of formed Ni-precipitates onto diatomite support (D) was carried out by the addition of hot (90°C) aqueous suspension of D to a slurry containing precipitates of Ni and Mg in molar ratio $\text{SiO}_2\text{:Ni}=1$. The obtained suspension was aged again for 1 h under the same temperature after which it was vacuum filtered and thoroughly washed with hot (80°C) distilled water until neutral pH. Finally, the precipitates were dried in an air oven at 110°C for 24 h and grounded to powder. After that, the samples were calcined at 550°C for 5 h. The same preparation procedure was employed for all the samples. The samples were designated as the NiMg/D-X (X=S-sulfamate, N-nitrate, or A-acetate) according to the kinds of nickel salts. The Ni content (weight percent) of the samples determined by the ICP-OES method for NiMg/D-S, NiMg/D-N, and NiMg/D-A were 35.0 wt.%, 36.3 wt. % and 36.6 wt. %, respectively.

3.1.2 Mixed oxides derived from layered-double hydroxalcite (LDH) materials

The co-precipitation method with sodium carbonate (Na_2CO_3) was carried out for the mixed oxides catalysts preparation based on the report [250]. The mixed oxides doped by different loading of yttrium were prepared. In detail, an aqueous solution of the following nitrates was used: Ni, Y, Al, and Mg, and added dropwise into Na_2CO_3 solution. NaOH (2 M) was also dripped into the mixture to adjust pH to 10 ± 0.2 . The ratio of $\text{M}^{2+}/\text{M}^{3+}$ was assumed as 3. The assumed loading of yttrium

was 0.4 wt.%, 2.0 wt.% or 4.0 wt.%. After co-precipitation, the suspension was left to react at 65 °C for 24 h. Then, this mixture was filtered under vacuum and washed with distilled water thoroughly. After filtration, the obtained cake was dried at 80 °C overnight and calcined in static air at 550 °C for 5 h with a heating rate of 5 °C/min. The samples were designated as MO-0Y, MO-0.4Y, MO-2.0Y, and MO-4.0Y. This work was done in the framework in collaboration with the AGH University.

3.1.3 Y-promoted novel ceria supported Ni catalysts

The catalysts were synthesized by a two steps method. First, CeO₂, Y₂O₃, and yttrium-promoted CeO₂ (denoted as CeO₂-YX%) supports were prepared by the hydrothermal method. In a typical procedure, 6 g of cerium nitrate, Ce(NO₃)₃·6H₂O (Aldrich, 99%) and an appropriate amount of yttrium nitrate hexahydrate, Y(NO₃)₃·6H₂O, (Aldrich, 99%) were dissolved in 30 mL of H₂O, then, 40 mL of NaOH (2.5 mol L⁻¹; Aldrich, >98%) were added to the solution under vigorous stirring. The resulting suspension was rapidly transferred into a 100 mL Teflon autoclave and heated in an oven at 120 °C for 24 h. After aging, the obtained precipitate was filtered and washed with deionized water until neutral pH. The resulting powder was dried at 80 °C overnight and calcined at 550 °C for 5 h in static air with a heating rate of 2 °C/min. The Y loadings with respect to CeO₂ are 0.5, 1.0, 2.0, 5.0 weight percent, respectively. CeO₂ and Y₂O₃ pure oxides were prepared by the same method, starting from Ce(NO₃)₃·6H₂O (Aldrich, 99%) or Y(NO₃)₃·6H₂O precursors.

The nickel catalysts were synthesized by the wetness impregnation method of the so prepared supports with an aqueous solution of Ni(NO₃)₂·6H₂O. After the impregnation process, the solids were dried at 100 °C overnight and calcined at 550 °C for 5 h with a heating rate of 2 °C/min. The

nickel loading for all the samples is 5 wt.%. The resulting catalysts were labeled according to the weight loading of Ni and Y, i.e., 5Ni/CeO₂, 5Ni/Y₂O₃, 5Ni/CeO₂-Y0.5%, 5Ni/CeO₂-Y1.0%, 5Ni/CeO₂-Y2.0%, and 5Ni/CeO₂-Y5.0%. The samples were synthesized in the framework of collaboration with Prof. Liotta from CNR Italy.

3.1.4 Ordered mesoporous SBA-15 and SBA-16 materials supported catalysts

The mesoporous materials including SBA-15 and SBA-16 were prepared by hydrothermal method using Teflon bottler or a PTFE lined stainless steel hydrothermal autoclave as shown in Annex 2.

SBA-15. Thus, SBA-15 was synthesized by the hydrothermal synthesis method as described by Han et al. [251]. In brief, Pluronic P123 (PEG-PPG-PEG, average molar weight=5800 g/mol, BASF) was dissolved in distilled water and the pH value of the aqueous solution was adjusted by adding HCl (37%, Sigma-Aldrich). After mixing thoroughly (45 min), TEOS (Tetraethyl orthosilicate, 98%, Sigma-Aldrich) was added dropwise to the above-mentioned solution and then stirred magnetically at 40 °C for 24 h. The molar ratio of the reaction mixture was controlled as TEOS/P123/HCl/H₂O=1/0.0168/5.8/155. The resulting mixture was aged at 65°C for 120 h. Then, the precipitate was filtered and washed with distilled water followed by drying in an oven at 110°C for 12 h. The obtained solids were calcined at 550 °C for 5 h in flow air (20 ml/min) with a heating rate of 1 °C/min.

3.1.4.1. Synthesis of NiY/SBA-15 and NiCexY/SBA-15 catalysts

Ni/SBA-15 catalysts doped by Y were prepared by a co-impregnation method in the presence of the surfactant cetyltrimethylammonium bromide (CTAB). The Y content (x) was controlled as 5, 10, and 20 wt.% relative to SBA-15 support. The Ni content was chosen as 15 wt.% for all samples. Typically, a certain quality of nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, >99%, Sigma-Aldrich), yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, >99%, Sigma-Aldrich), and CTAB (>99%, Sigma-Aldrich) were dissolved in distilled water and magnetically stirring for 30 min. Subsequently, the SBA-15 powder was added to the prepared solution and the magnetic stirring was maintained for 12h at ambient temperature. The CTAB/Ni molar ratio was controlled at 0.3. Afterward, the obtained slurry was evaporated in a rotary evaporator (60°C, 110r/min). After that, the material was dried in an oven at 100 °C for 12h and calcined at 550 °C under flow air for 5h with a heating rate of 5 °C/min (20 mL/min).

NiCe/SBA-15 catalysts modified with Y were prepared by the same technique as NiY/SBA-15 with the presence of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, >99%, Sigma-Aldrich). The yttrium content (x) in the NiCexY/SBA-15 catalysts varied from 2 to 10 wt.%, whereas a fixed amount of Ni (15 wt.%) and Ce (10 wt.%) was adjusted. The as-prepared catalysts were labeled as 15Ni10Ce/SBA-15 and 15Ni10CexY/SBA-15 (x= 2, 4, 10).

3.1.4.2. Synthesis of SBA-16 supports

SBA-16 materials were synthesized based on an improved method presented elsewhere [252]. Typically, 3 g of Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) copolymer (BASF) was dissolved with 144 g of distilled water in a Teflon bottle followed by adding 5.94 g of concentrated hydrochloric acid (HCl, 37 wt.%, Sigma Aldrich). After stirring for 20-30 min, 9 g of butanol-1 (BuOH, Sigma

Aldrich) was added into the aforementioned solution as a co-surfactant. The molar ratio of F127/BuOH was controlled as 1/3. After stirring for 1 h, 14.2 g of tetraethyl orthosilicate (TEOS, Sigma Aldrich) was added into the solution above at 40 °C, then the mixture was kept at 40 °C for 24 h. Afterward, the container of the solution was placed under a static condition (electrical oven) at 80 °C for 48 h for the hydrothermal process. After that, the mixture was filtered and washed by distilled water thoroughly. Subsequently, the precipitant was dried at 100 °C for 12 h. Finally, the solid was calcined at 550 °C for 5 h with a heating rate of 5 °C/min under flowing air (20 mL/min) to remove the copolymer template F127.

3.1.4.3. Ni/xCe/SBA-16 catalysts preparation

Ni/SBA-16 and Ce-promoted Ni/Ce/SBA-16 catalysts with different Ce content were prepared by a two-step incipient wetness impregnation method assisted by ultrasonic considering its advantages compared to the co-impregnation method [253]. As reported in the literature, the Ni-Ce/SBA-15 catalyst prepared by impregnating of Ce then by Ni presented smaller NiO particles and porosity compared with the co-impregnated catalyst and the catalyst impregnated first by Ni [254]. In the current work, cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, >99%, Sigma-Aldrich) was dissolved in distilled water, and then the SBA-16 support was added into the solution. The suspension was processed by ultrasonic for 1 h, after that, the mixture was placed at ambient temperature for 24 h to optimize the diffusion of ions inside the pores of the support. Afterward, the mixture was dried at 80 °C for 12 h. Finally, the material was calcined in an electrical furnace at 550 °C for 5 h with a heating rate of 5 °C/min in airflow (20 mL/min). Eventually, the as-synthesized SBA-16 and Ce/SBA-16 were used to prepared Ni/SBA-16 and Ni/Ce/SBA-16 catalysts. The same

impregnation method was used to prepare the catalyst, with replacing the solvent with ethanol (99%), which showed better performance for supported Ni catalysts relative to H₂O [255]. The content of Ni was 10 wt.% relative to the support. The catalysts were then designated as 10Ni/SBA-16 or 10Ni/xCe/SBA-16, where x represents the content of Ce, varying from 10 to 20 wt.%. All the reagents were purchased from Sigma-Aldrich or BASF (F127).

3.1.4.4. Synthesis of Ni/xCeY/SBA-16 catalysts

The Ni/xCeY/SBA-16 catalysts were prepared by a two steps impregnation method as introduced above. Firstly, the xCeY/SBA-16 materials were prepared by wet impregnation of an aqueous solution of nitrate salts (Ce(NO₃)₃·6H₂O, Y(NO₃)₃·6H₂O, >99%, Sigma-Aldrich) on SBA-16. After impregnation, dry, and calcination, the obtained xCeY/SBA-16 samples were impregnated by the ethanol solution of Ni(NO₃)₂·6H₂O with/without the presence of citric acid (>99%, Sigma-Aldrich). The final catalyst precursors were obtained after subsequent impregnation, dry, and calcination. The weight content Ce and Ni was 10 wt.% with Y content varying from 2 to 10 wt.%. The samples were denoted as 10Ni/10Ce/SBA-16 and 10Ni/10CexY/SBA-16, respectively. The 10Ni/SBA-16 sample was also prepared by the same process as a reference.

3.2 Catalytic CO₂ methanation

3.2.1 Activity test

The catalytic test was carried out in a fixed-bed reactor (Inner diameter of 10 mm). The catalyst (0.5 mL, density measured by a measuring cylinder of 5 mL) was loaded into the reactor under the

protection of quartz wool. A K-type thermocouple in contact with the catalyst bed was used to monitor the temperature. Before the test, the catalyst was pretreated in a gas mixture of Ar and H₂ (H₂/Ar=5%, vol./vol.) with a flow rate of 100 mL/min for 1 h. After reduction and cooling down to the desired temperature, the activity test was performed from 200 to 450 °C in a reactive gas mixture (CO₂/H₂/Ar=60/15/25, 100 mL/min) with a temperature ramp of 10 °C per min (Fig.3.2a). At each step, the temperature was kept for 30 min for the steady-state test. The gas/weight hourly space velocity (GHSV/WHSV) is 12, 000 h⁻¹ (per hour)/60, 000 g_{cat}⁻¹•h⁻¹(per gram of catalyst per hour). The outlet gases were analyzed by a gas chromatograph equipped with a thermal conductivity detector (TCD) (490 Varian Micro-GC) from Agilent.

The time-on-stream (TOS) test was performed on the same set-up. The feed gas with the same composition was fed into the catalyst after the reduction step. As shown in Fig.3.2b, the isothermal test was carried out at 350 °C and kept for 6-7 h.

The design drawing and the assembled real profile of the set-up were shown in Fig.3.3.

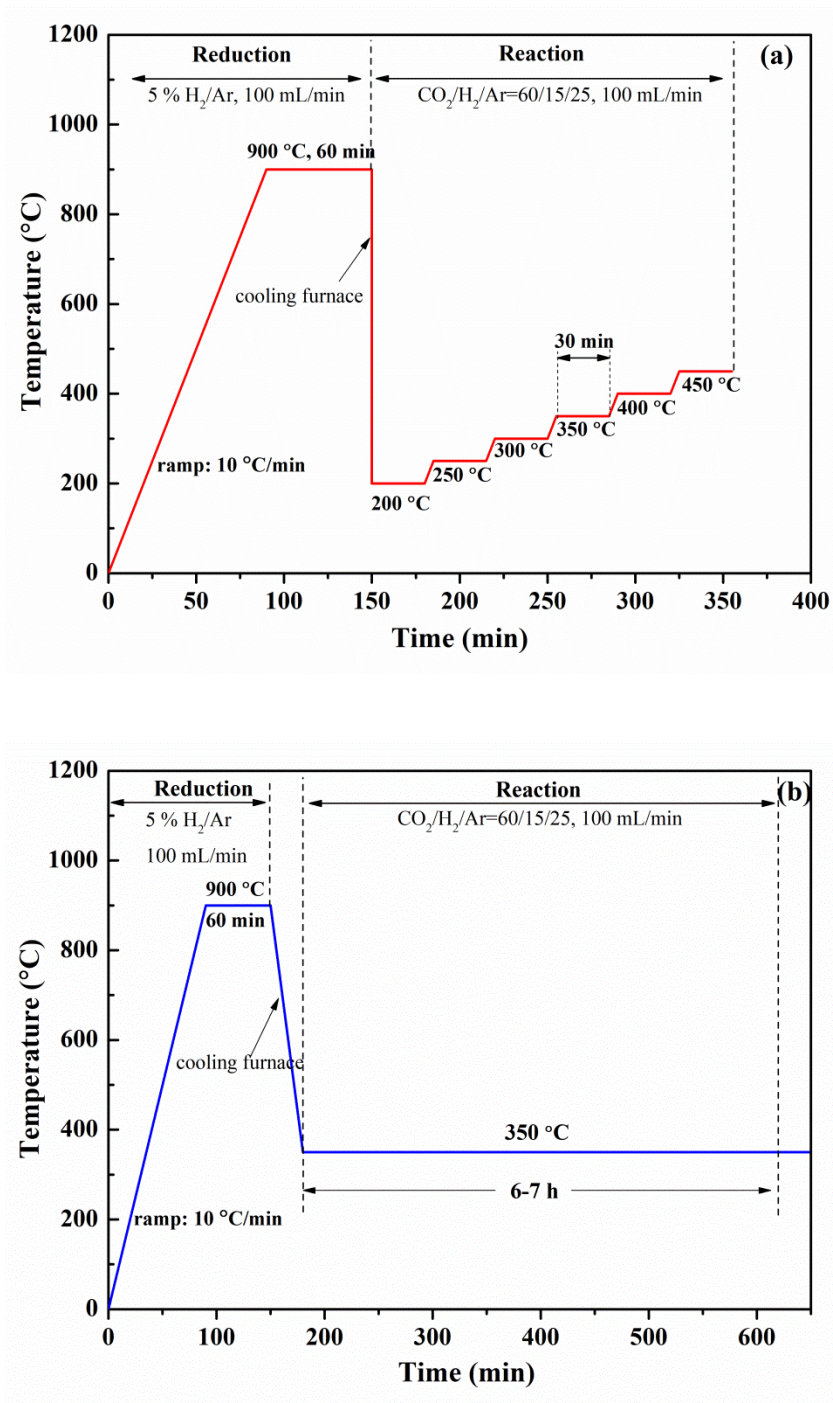


Figure. 3.2. Temperature programs used in activity test (a) and isothermal test of time-on-stream (b) for CO₂ methanation.

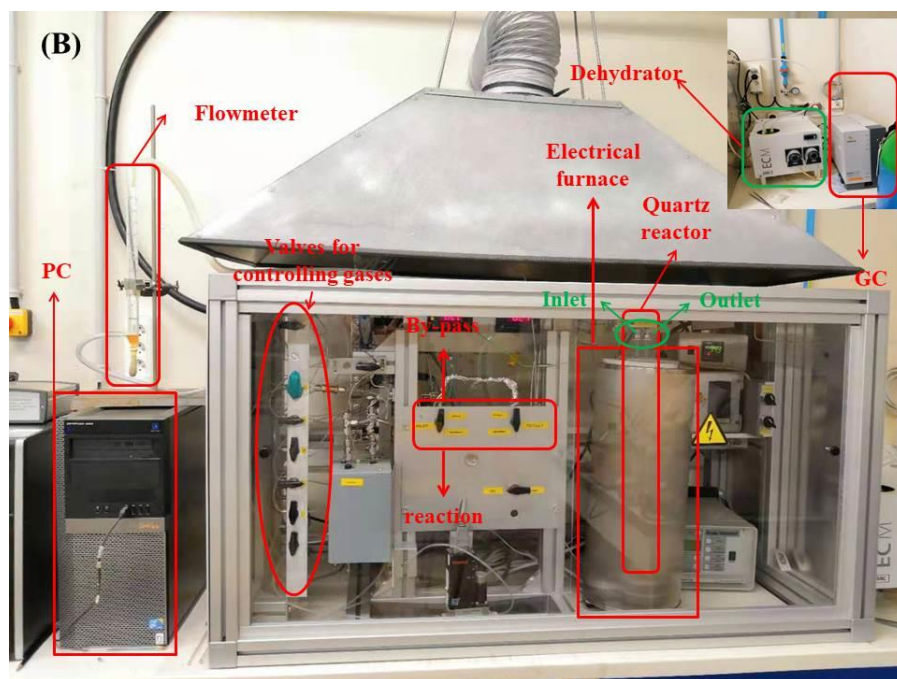
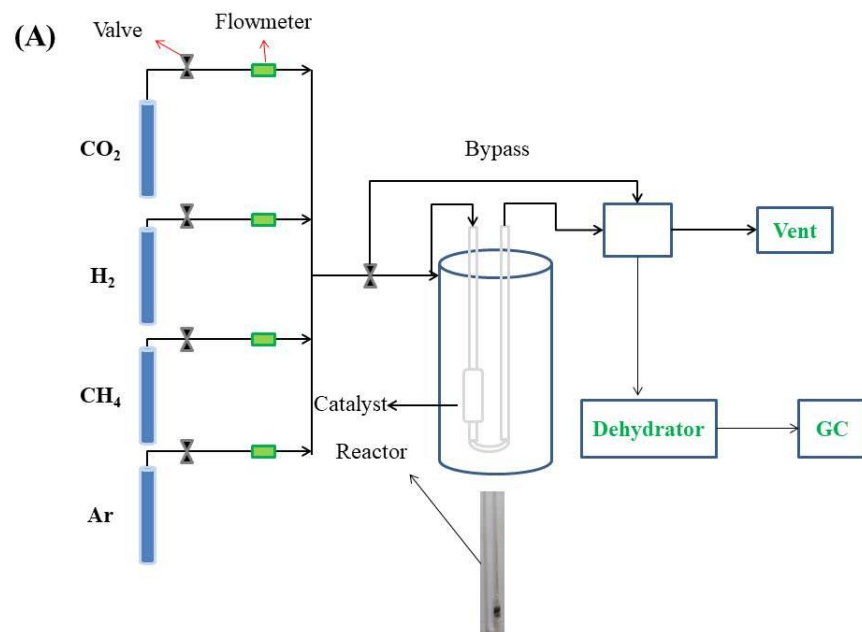


Figure. 3.3. Scheme (A) and real profile (B) for the CO₂ methanation set-up.

3.2.2 Calculations

The CO₂ conversion (X_{CO₂}) and CH₄ (S_{CH₄}) selectivity were calculated by the following equations:

$$X_{CO_2} (\%) = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} = \frac{n_{CO_2, in} \times Q_{in} - n_{CO_2, out} \times Q_{out}}{n_{CO_2, in} \times Q_{in}} \times 100 \quad (\text{Equation 1})$$

$$S_{CH_4} (\%) = \frac{[CH_4]_{out}}{[CO_2]_{in} - [CO_2]_{out}} = \frac{n_{CH_4, out} \times Q_{out}}{n_{CO_2, in} \times Q_{in} - n_{CO_2, out} \times Q_{out}} \times 100 \quad (\text{Equation 2})$$

Which the [CO₂]_{in} and [CO₂]_{out} represent the gas molar flow of CO₂ in inlet and outlet, respectively; [CH₄]_{out} is the gas molar flow of CH₄ in the outlet; the n_{CO₂, in} and n_{CO₂, out} refers to the molar concentration of CO₂ in inlet and outlet, respectively. The Q_{in} and Q_{out} represent the flow rate measured by a flowmeter (Fig. 3.3b) of inlet and outlet, respectively.

The gas hourly space velocity (GHSV, h⁻¹) of weight hourly space velocity (WHSV, mL/g_{cat}·h⁻¹) value was calculated following the equation below (Equation 3 and 4):

$$GHSV (h^{-1}) = \frac{\text{Total volumetric flow rate of the inlet gases}}{\text{Volume of the loaded sample}} = \frac{Q_{in}}{V_{cat}} \quad (\text{Equation 3})$$

$$WHSV (g_{cat} \cdot h^{-1}) = \frac{\text{Total volumetric flow rate of the inlet gases}}{\text{weight of the loaded sample}} = \frac{Q_{in}}{m_{cat}} \quad (\text{Equation 4})$$

TOF (S⁻¹) value was calculated supposing that all the exposed Ni atoms participate in the reaction using the following equation (Equation 5)

$$TOF(S^{-1}) = \frac{n_{CH_4}(mol)}{n_{Ni}(mol) \cdot t(s)} \quad (\text{Equation 5})$$

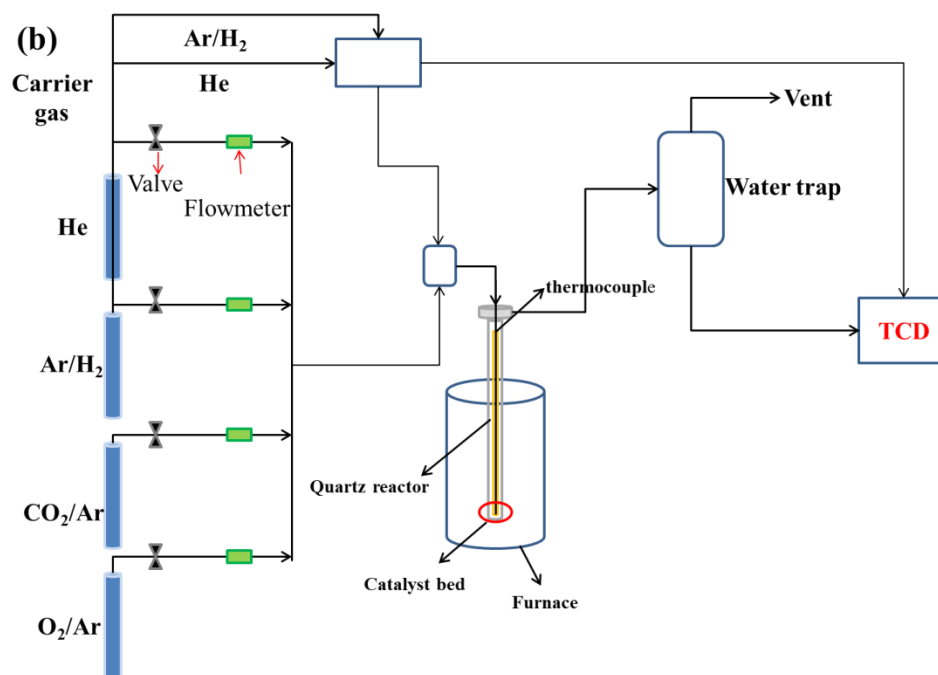
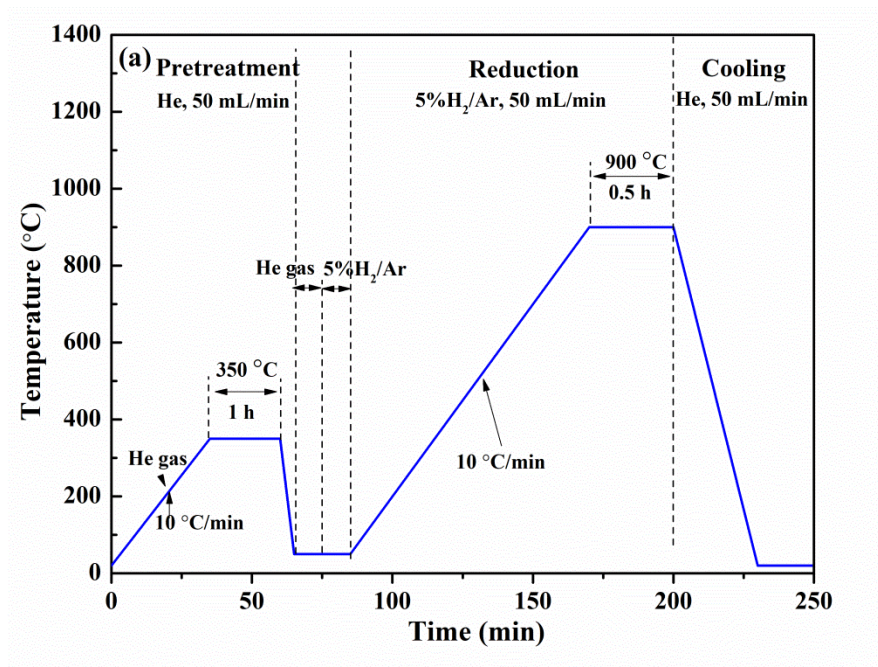
3.3 Characterization of the supports and catalysts

3.3.1 Temperature-programmed reduction in hydrogen (H₂-TPR)

In order to study the reducibility, metal particle distribution, and metal-support interaction [250,256], etc. of the catalyst or support, the temperature-programmed reduction in hydrogen (H₂-TPR) experiment was carried out for supports and catalysts. As the difference of interaction intensity between metal oxides and support and the particle size of crystallite, the metal oxides can be reduced by H₂ at different temperatures. Besides, some materials like CeO₂ and ZrO₂ can also be reduced by H₂ due to their redox properties [257].

The experiment program, scheme, and set-up used in this thesis were shown in Fig.3.4. The apparatus from BEL Japan Inc. shown in Fig.3.4c was equipped with a thermal conductivity detector (TCD).

As shown in Fig.3.4a, the sample was pretreated at 350°C by helium (He) to blow out the impurities adsorbed on the surface of the sample before reduction. After pretreatment, a gas mixture of 5% H₂/Ar was fed into the sample. When the baseline of the TCD signal was stable, the sample was heated to 900 °C (ramp: 10 °C/min) and kept at 900 °C for 30 min. At last, the furnace was cooled down to ambient temperature.



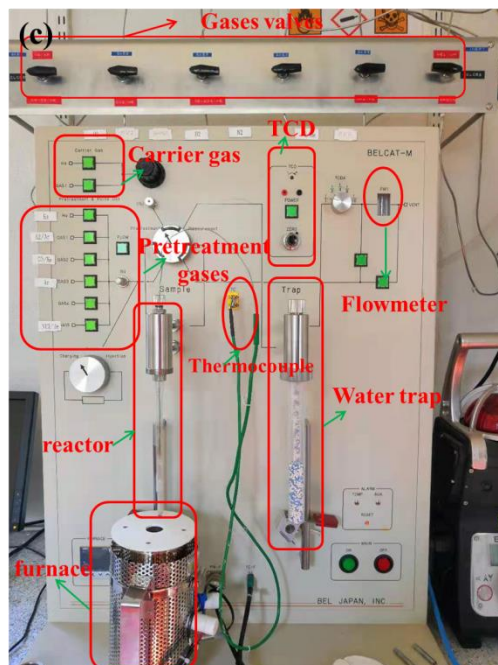


Figure. 3.4. Experimental program (a), scheme (b), and set-up (c) used in the TPR process.

3.3.2 Temperature-programmed desorption in CO₂ (CO₂-TPD)

To obtain the basicity and CO₂ adsorption ability on the surface of the sample, temperature-programmed desorption in CO₂ (CO₂-TPD) experiment was performed. This technology allows getting the total basicity and basic site distribution of the samples. According to the desorption temperature, the basic sites were divided into 3 types i.e. weak ($T < 150\text{ }^{\circ}\text{C}$), medium ($T = 150\text{--}550\text{ }^{\circ}\text{C}$), and strong basic sites ($T > 550\text{ }^{\circ}\text{C}$) [160,208,258,259]. The weak basic sites are attributed to CO₂ desorption from adsorbed CO₂ on the surface hydroxyl (OH⁻) species [258,259]. The medium was assigned to Lewis acid-base pairs [258]. The strong basic sites were attributed to bulk carbonate decomposition [258,260]. Given the FTIR results reported, the weak, medium, and strong basic sites were caused by the chemisorbed CO₂ in the form of bicarbonate, bidentate carbonate, and unidentate carbonate, respectively [260].

The TPD experiments were carried out in the same apparatus as TPR and the scheme of the experiment was shown in Fig.3.5. At first, the sample was reduced at the desired temperature (550 °C) for 1 h under a gas mixture of 5% H₂/Ar (50 mL/min). Then, the reduced sample was cooling down under H₂ to 50 °C and blew by He to clean the surface followed by the adsorption of CO₂ at the same temperature (10% CO₂/Ar, 50 mL/min). After that, the adsorbed CO₂ was blown by He (50 mL/min). At last, the TPD process was performed from 50 to 900 °C under He.

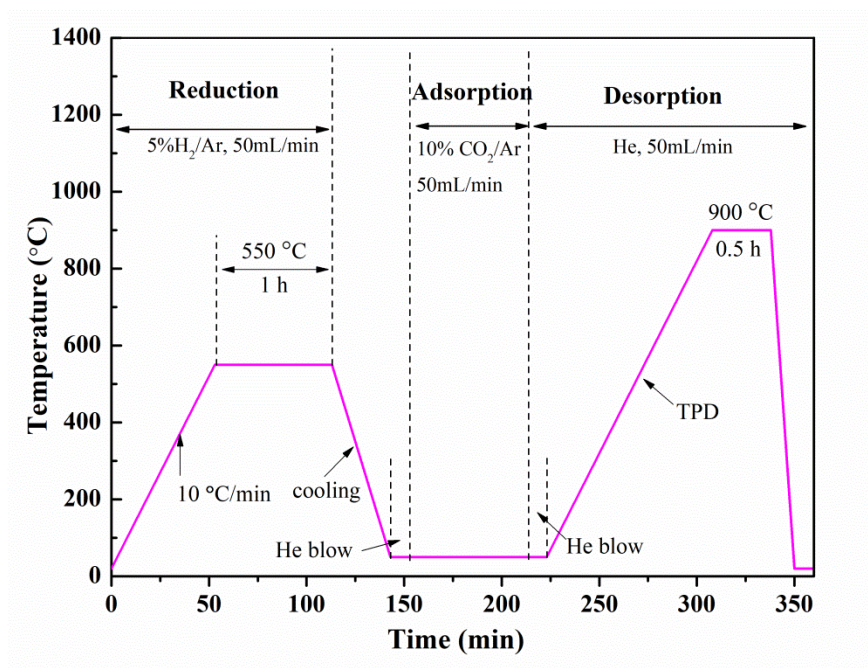


Figure. 3.5. The experimental program of temperature-programmed desorption of CO₂ (CO₂-TPD).

3.3.3 Physical adsorption of nitrogen (N₂)

The physical adsorptions of nitrogen (N₂) experiments were carried out to obtain the textural properties like specific surface area (SSA), pore volume (V_p), and average pore size (D_p). The experiments were performed in a Belsorp Mini II apparatus (Fig.3.4) from BEL Japan Inc. Before measurement, the sample was degassed at 200 °C under vacuum conditions for 4 h. After that, the

N₂ physical adsorption was carried out under liquid N₂ temperature (-196 °C). The SSA was calculated by the Brunauer-Emmett-Teller method (BET) using equation 6 [261,262]:

$$\frac{p}{V(p_0-p)} = \frac{(c-1)}{VmC} \times \frac{p}{p_0} + \frac{1}{VmC} \quad (\text{Equation 6})$$

$$S_g = \frac{V_m N_A A_m}{2240W} \times 10^{-18} \quad (\text{Equation 7})$$

$$S_g \text{ (m}^2\text{/g)} = 4.36 \times V_m / W \quad (\text{Equation 8})$$

P represents the partial pressure of N₂ (Pa); P₀ represents the saturated vapor pressure of liquid N₂ (Pa) at adsorption temperature; V_m is the monolayer adsorbed gas quantity (mL); V is adsorbed gas quantity; C is BET constant. S_g is the SSA of the sample (m²/g); N_A is Avogadro's constant (6.02×10²³); A_m is the Equivalent maximum cross-sectional area of N₂ molecules (0.162 nm²); W is the weight of the sample (g). When the N₂ is used as adsorbate, the S_g can be calculated by equation 7.



Figure. 3.6. BELSORB MINI Apparatus used in the physical adsorption of nitrogen (N₂).

The pore volume and average pore diameter were calculated by the Barrett-Joyner-Halenda (BJH) method, which implements two fundamental assumptions i.e. the shape of the pore is cylindrical, and the adsorbed amount results from both physical adsorption on the pore walls and capillary condensation in mesopores [263]. Pore size distribution (PSD, nm) uses the classical Kelvin equation (equation 9);

$$\ln \frac{P}{P_0} = \frac{2\gamma V_m}{rRT} \quad (\text{Equation 9})$$

where P/P_0 is the relative pressure; γ is the surface tension of the adsorbate in the liquid form (N_2); V_m (mol/L) is the molar volume of the liquid; R is the universal gas constant; r is the radius of the meniscus formed in the mesopore; T is temperature [263,264].

N_2 physisorption isotherms can be classified into 6 types (Fig.3.7). As shown in Fig.3.7, the type I isotherm, also called Langmuir isotherm, was assigned to the adsorption in which pores were filled at low relative pressure with a cliffy uptake owing to the significant adsorbent-adsorbate interaction [263]. The type II isotherm normally happens on the non-porous materials and macroporous materials, where N_2 molecules are absorbed in mono/multi-layers without restriction [263]. The type IV isotherm that has a hysteresis loop is often found on materials with micropores and mesopores in which capillary condensation happens due to the interactions between gas molecules and adsorbent mesopore surface [263]. The type III and V isotherms with initial zero slopes correspond to weak adsorbate-adsorbent interactions on the materials (e.g. polyethylene). Type VI refers to stepwise multilayer adsorption on a uniform non-porous surface that usually happens on graphite carbon [263].

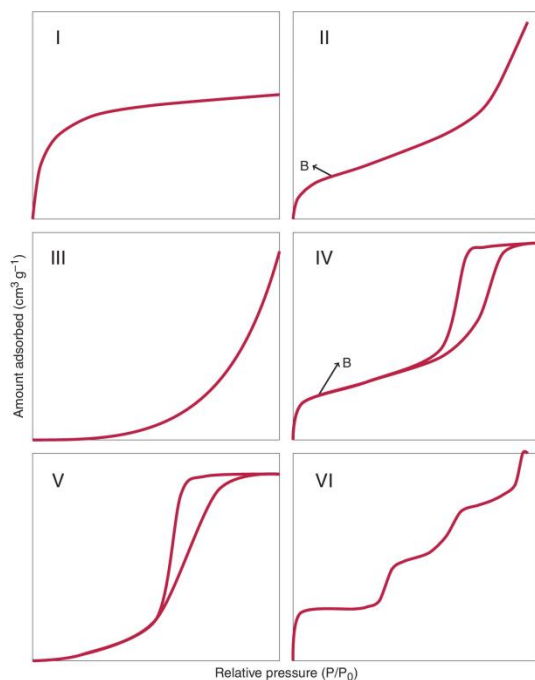


Figure. 3.7. The N₂ adsorption-desorption isotherms; Adapted from [263].

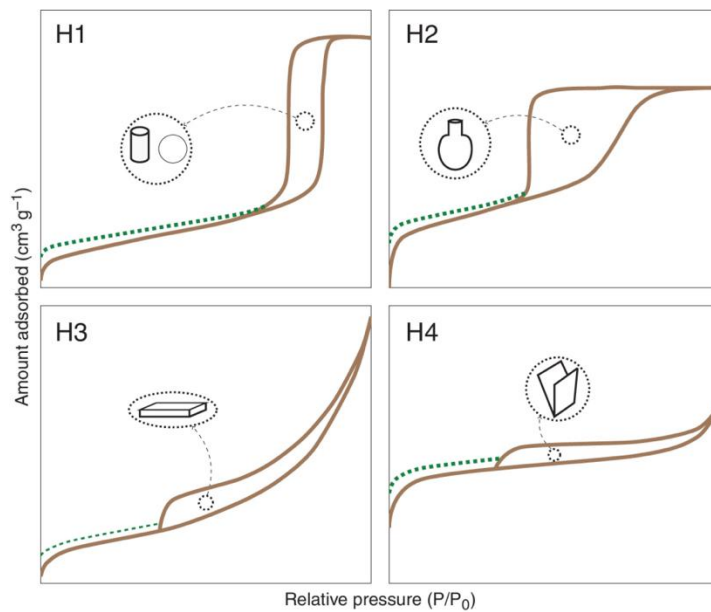


Figure. 3.8. Types of hysteresis loops obtained by N₂ physisorption; Adapted from [263].

According to the occurrence of capillary condensation in mesopores, the desorption isotherm is different from the adsorption one resulting in the formation of hysteresis loops. The loops consist

of 4 types as shown in Fig.3.8, which are associated with the pore shapes. The H1 is attributed to the uniform distribution of spherical and cylindrical narrow mesopores. H2 exists in inorganic oxides with a complex network of interconnected narrow pores. H3 are found in materials that have aggregated non-rigid plate-like particles (e.g. clay) [265]. Type H4 is characteristic of microporous materials that have narrow slit-like pores with type I isotherms [263].

Besides the BJH method, PSD (nm) is also often calculated by density function theory (DFT). The equation is below:

$$N_{\text{exp}}(P/P_0) = \int_{D_m}^{D_M} N_{\text{DFT}}\left(\frac{P}{P_0}, D\right) \times f(D) dD \quad (\text{Equation 10})$$

Where $f(D)$ is an unknown PSD function; D_m and D_M correspond to the minimum and maximum pore sizes in the kernel, respectively [263].

3.3.4 Chemisorption of hydrogen (H₂ chemisorption)

In order to obtain the active metal distribution, the H₂ chemisorption was employed to determine nickel dispersion (Micromeritics, ASAP 2020). Before analysis, about 0.2 g of calcined sample was evacuated in helium at 40°C. The sample was subsequently reduced in situ at 550°C for 1.5 h in the flow of H₂ (30 mL/min). The temperature was cooled down to 40°C, followed by the volumetric H₂ chemisorption with pure hydrogen. The metal distribution (D) is calculated by the following equation [266]:

$$D (\%) = \frac{1.17X}{W_f} \quad (\text{Equation 11})$$

The average nickel crystallite diameter (surface-averaged, nm) was calculated using the equation 12 [266]:

$$d_{\text{Ni}} (\text{nm}) = \frac{971}{D} \quad (\text{Equation 12})$$

Where the X is chemisorbed H₂ in micromoles per gram of catalyst, W represents the weight percentage of Ni, and f is the fraction of Ni reduced to the metal.

The Ni surface area was calculated by assuming that one hydrogen atom corresponds to one Ni atom and that the cross-sectional area of the Ni atoms is $6.49 \times 10^{-20} \text{ m}^2$ [267].

3.3.5 X-ray diffraction (Small-angle and Wide-angle)

To obtain the structural properties e.g. phase composition and crystallite size of the samples, the X-ray diffraction technologies including small-angle and large-angle (SAXRD and WAXRD) were performed for the studied materials. The SAXRD was used to confirm the ordered structure of the ordered mesoporous materials. The samples after calcination (550 °C, 5 h), reduction, and catalytic tests were characterized by WAXRD experiments.

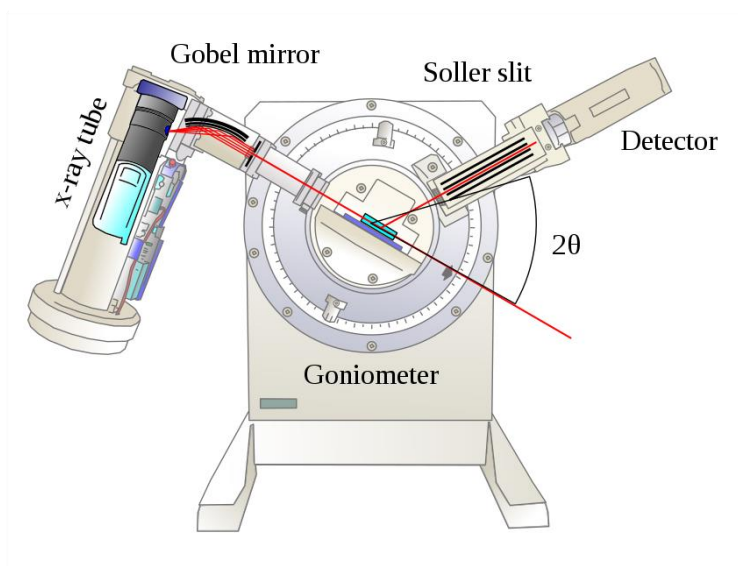
XRD measurements were carried out on PANalytical-Empyrean diffractometer equipped with Cu K α ($\lambda=1.5406\text{\AA}$) radiation source, with the scanning range of 2 theta (θ) range from 5 to 90°, with a 0.02°/min step size. The WAXRD experiments were carried out with the 2 θ range of 0.5-6.0° by a stepwise of 0.01°. Fig.3.8 shows a set-up, schematic diagram, and principles of X-ray diffractometer with main components.

The average crystallite size (D, nm) of Ni metal and support were calculated by Scherrer equation:

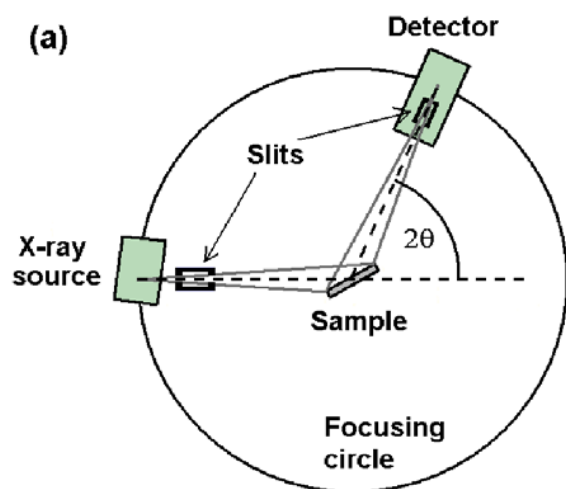
$$D_{hkl}(nm) = \frac{K\lambda}{\beta_{hkl}\cos\theta} \quad (\text{Equation 13})$$

In which k is Scherrer parameter (0.9); λ is the radiation wavelength ($\lambda=1.5406\text{\AA}$), β_{hkl} refers to the full width at half maximum of the reflection peak, and θ represents the Bragg diffraction angle.

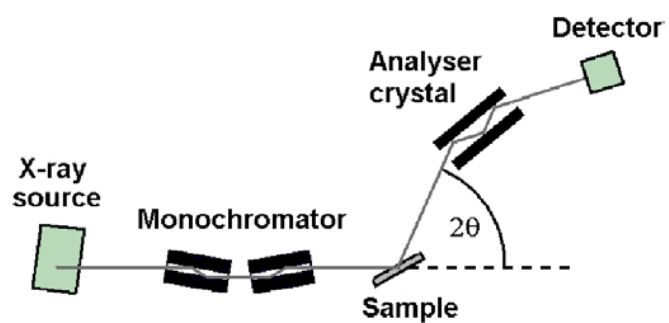
(A)



(B)



(b)



(C)

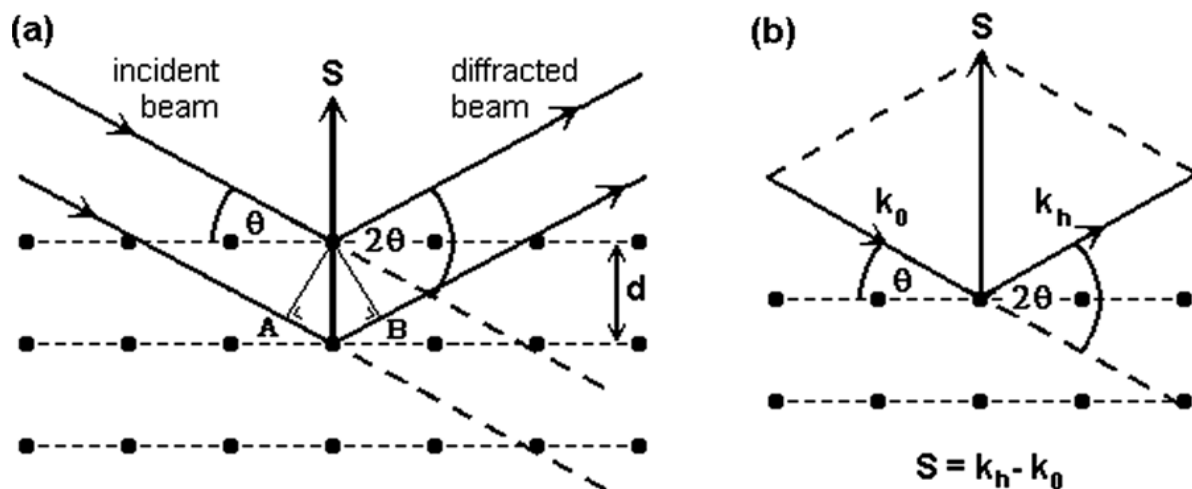


Figure. 3.8. A set-up (A), schematic diagram (B), and principles (C) of x-ray diffractometer with main components;

Adapted from [268]

3.3.6 Elemental composition analysis

To obtain the element composition of catalysts, the X-Ray Fluorescence (XRF) in a Rigaku Supermini200 analyzer or XRF 1800 Shimadzu was used to evaluate the elemental composition of the studied catalysts. The experiment was performed under vacuum at 36.5 °C in the presence of P-10 gas (a mixture of 10% CH₄/Ar, flow 24.7 mL/min). A pulse height analyzer was used to calibrate the proportional counter (PC) detector. The calcined sample was homogeneously mixed with boric acid and pelletized under 10 bar. So prepared pellet was then covered by polypropylene film (6 μm) and put into a sample holder for analysis.

3.3.7 Transmission electron microscopy and Energy Dispersive X-ray spectroscopy

To acquire the morphology information and metal size of the catalyst, the Transmission electron microscopy (TEM) and Energy Dispersive X-ray spectroscopy (EDX) analyses were carried out with JEM-2010 and JEM-2100Plus (JEOL, Tokyo, Japan) transmission electron microscopes for the reduced catalysts. Before measurement, the reduced samples were dispersed in ethanol, following the suspension being added dropwise on a copper grid covering with carbon film, then the prepared materials were used for the microscopy measurement.

3.3.8 X-ray photoelectron spectroscopy

To obtain the surface compositions and oxidation states of the catalysts, the X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Microtech ESCA 3000Multilab spectrometer, equipped with a dual Mg/Al anode, with an excitation source of unmonochromatized Al K α radiation (1486.6 eV). The sample powders as received were analyzed as pellets, mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10^{-8} Torr during data collection. The constant charging of the samples was removed by referencing all the energies to the Ce3d_{5/2} component at 882.1eV or C1s peak to 284.6 eV. Quick scans of the Ce3d region were performed before each analysis to evaluate possible reduction under the beam. Analyses of the peaks were performed with the software CasaXPS. Atomic concentrations were calculated from peak intensity using the sensitivity factors provided by the software. The binding energy values are quoted with a precision of ± 0.15 eV and the atomic percentage with a precision of ± 10 %.

3.3.9 Thermogravimetric analyses-mass spectrometer (TGA-MS)

To obtain the information of possible carbon deposition on the spent catalysts, the thermogravimetric analysis (TGA) was performed on the spent catalysts by the Q5000 IR apparatus. Around 25 mg of material was heated starting from room temperature to 750 °C (heating rate of 10 °C/min). The measurements were performed in synthetic air. The amount of H₂O and adsorbed CO₂ were estimated by the mass loss registered in the TGA plots and mass spectrometer (MS) signal.

3.3.10 Temperature-programmed oxidation (TPO)

To investigate the possible surface carbon deposition effects on the catalysts, the temperature-programmed oxidation (TPO) analyses were carried out on the spent catalysts by Quadstar Mass equipped with a Pfeiffer Vacuum. Around 30 mg of a sample was heated from ambient temperature to 800 °C with a heating rate of 5 °C/min. The measurements were performed in a 5% O₂/Ar gas mixture (Volumetric percentage, 200 ml/min). During the mass spectroscopy analysis, the following desorbed species were recorded; mass-to-charge ratio (m/z): 44 (CO₂) and 18 (H₂O). The CO₂ signal in the graph was enlarged 10 times for the analysis.



Chapter IV

Low-cost materials for CO₂ methanation

4. Low-cost materials for CO₂ methanation

4.1 Ni-Mg catalysts supported on diatomite

4.1.1 Introduction

In the past decades, climate changes caused by global warming had brought about serious impacts on the natural system and human society [15]. The reduction of CO₂ emissions has gained legislative importance [33]. The greenhouse gases e.g. CO₂, CH₄, and nitrous gases, mainly come from industrial activities and population growth. CO₂ emission, which mainly comes from fossil fuel consumption, accounts for most greenhouse gas emissions [269]. To mitigate climate change, the reduction of CO₂ emissions is important to protect the environment and achieve sustainable development [4,15]. It is impossible for human societies to stop consuming fossil fuels soon. Thus, the technologies to capture, store, and utilize CO₂ from the atmosphere or industrial plants would bring both economic and environmental benefits [270,271].

CO₂ reduction technologies can be divided into CO₂ capture and storage (CCS) and CO₂ capture and utilization (CCU) routes [272]. The CCU technologies consist of chemical and biological methods in which the chemical methods show the most potential now [38]. Catalytic CO₂ conversion routes to fuels and chemicals e.g. methane, methanol, or dimethyl ether received much interest due to their high value [3,4,269]. They can not only provide an alternative route to reuse the fossil carbon resources and closed the anthropogenic carbon cycle but also synthesized high-value chemicals and fuels [3]. CO₂ hydrogenation into methane over transition metal-based catalysts using renewable hydrogen from water electrolysis as an example has a huge potential to reduce the emissions and, at the same time, to store the excess renewable energy to equalize the

demand and capacity in a power to gas (PtG) process, which a few plants were already operated in European Union [100,165,230,273,274].

CO₂ methanation, also called Sabatier reaction, i.e. $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ ($\Delta G_{298\text{K}} = -130.8$ kJ/mol), was a thermodynamically favorable and exothermic reaction [98]. Compared to other chemical reactions of CO₂ conversion, it showed more feasible potentials towards commercialization due to the high activity and moderate running conditions [7]. Moreover, the resulting CH₄ or synthetic/substitute natural gas (SNG) can be directly injected into the existing infrastructure for storage, transportation, and usage [7,137,167]. However, the presence of appropriate catalytic systems is indispensable due to the kinetic barriers [126].

Transition metals mainly VIII metals such as Rh, Ru, Pd, Co, Ni, Pt, and Fe [71,119,230,275–283,121,122,124,137,145,164,210,228] have been used for the formulation of supported metal catalysts. The noble metal-based catalysts like Rh and Ru showed high low-temperature activity and long-term stability, but their high cost limits the utilization on an industrial scale [258,284]. The Ni-based catalysts are much suitable due to their excellent CO₂ conversion and CH₄ selectivity, high availability, and low cost compared to the noble metal catalysts [123,137,288,289,145,167,274,279,280,285–287]. However, Ni-based catalysts still have drawbacks like poor stability, sintering of active metals, or chemical poisoning [173].

Numerous efforts have been devoted to promoting the activity and stability of Ni-based catalysts. The doping of other metals in the preparation of Ni-based catalysts e.g. Fe, Ce, Y, and Mg, etc. [142,144,290,291] had been reported to enhance the activity and stability of Ni-based catalysts towards methanation. Among the dopants, Mg seems to be a good modifying promoter since it affects the activation of CO₂ on Mg²⁺ and promotes the dispersion of Ni particles on the support, resulting in improved stability and carbon resistance [179].

Besides, the support also plays a decisive role in the metal-support interaction, which determined significantly the catalytic performance in CO₂ methanation [179]. Many materials such as SiO₂, Al₂O₃, TiO₂, CeO₂, ZrO₂ [141,147,168,173,214] have been used for the preparation of Ni-based catalyst for CO₂ methanation. It is proposed to design a Ni-based catalyst with special structures such as hydrotalcite and perovskite, which have a very high thermal stability against sintering [179,292]. Diatomite is a natural siliceous, porous, low density, hydrophobic material with high adsorption ability and thermal stability [293].

Diatomite had been used in the synthesis of catalysts for different applications as described in Table 4.1.

Table 4.1 Possible applications for Diatomite materials used as catalysts

Number	Reaction	Reference
1)	CO oxidation	[294]
2)	Degradation of organic pollutants	[295]
3)	Transesterification of vegetable oil	[296]
4)	Hydrogenation of vegetable oils	[297]
5)	Photocatalytic activity	[298,299]
6)	Heck and Suzuki reactions	[300]

However, until now the application of diatomite-supported nickel catalysts for CO₂ methanation has not been attempted. Therefore, for the first time, the capability of diatomite-supported Ni catalyst for CO₂ methanation was investigated.

The present chapter aimed to investigate the effect of three different nickel precursor salts on the textural, phase-structural, reducibility, and basicity properties of diatomite supported Ni-Mg catalysts obtained by the same precipitation-deposition (PD) method, as well as their catalytic performance in the CO₂ methanation.

4.1.2. Catalyst preparation and Physicochemical techniques

The detailed preparation process was depicted in 3.1.1 of chapter 3. The calcined samples were denoted as Ni-Mg/D-S, Ni-Mg/D-N, and Ni-Mg/D-A (X=S-sulfamate, N-nitrate, or A-acetate) based on the nickel precursors.

The textural properties of reduced and spent catalysts were analyzed by N₂ adsorption-desorption in a BELSORP Mini II-BEL Japan instrument. Before measurement, the samples (60 mg) were degassed at 200 °C for 2 h aiming at cleaning the surface, then the measurement was conducted at liquid N₂ temperature.

The structural parameters of catalysts (reduced and after methanation) were examined by X-ray diffraction (XRD) method in a PANalytical-Empryean diffractometer equipped with Cu K α radiation source ($\lambda=1.5406 \text{ \AA}$) within 2θ range from 10 to 90°, with a step-size of 0.02°/min. The reduced samples were obtained from the same reduction condition as the reaction, after the reduction, the samples were cooled down under Ar flow (100 mL/min) to ambient temperature. The reducibility of catalysts was studied by H₂-TPR by a BELCAT-M type (BEL Japan Inc.) set-up equipped with a conductivity detector (TCD). The samples (60 mg) were pretreated in helium (50 mL/min) at 100 °C for 2 h, and then the TPR experiment was carried out in a 5% H₂/Ar mixture (50 mL/min) up to 700 °C by a heating rate of 10 °C/min.

The basicity distribution of samples was measured by CO₂-TPD in the same apparatus as TPR-H₂, and the sample after TPR was pretreated by He at 80 °C for half an hour following the adsorption of CO₂ (10% CO₂/He, 50 mL/min) for 1 h, then the TPD was performed after desorbing the physically adsorbed CO₂ in 30 min at 80 °C.

4.1.3 Texture properties and structural parameters of catalysts

The textural properties of reduced and spent catalysts were displayed in Table 4.1. It can be seen from Table 4.1 that the highest specific surface area (SSA) was obtained on both reduced and spent Ni-Mg/D-N samples compared to the other two samples.

Table 4.1 BET specific surface area, pore volume and mean pore size of the catalysts

Sample	^a SSA [m ² g ⁻¹]		^b V _p [cm ³ g ⁻¹]		^c r _p [nm]		^d d _{Ni} [nm]	
	reduced	spent	reduced	spent	reduced	spent	reduced	spent
Ni-Mg/D-S	48.4	54.4	0.12	0.26	2.1	1.6	10.9	8.5
Ni-Mg/D-N	81.0	73.3	0.11	0.20	1.9	1.9	11.1	8.5
Ni-Mg/D-A	42.9	45.0	0.10	0.10	1.9	1.2	11.5	8.1

^a Calculated from BET method

^{b,c} Calculated from BJH method

^d Calculated from the three strongest peaks of XRD by Scherrer equation

Moreover, no large differences regarding SSA were observed between the reduced and spent catalysts, indicating that the surface of catalysts was not modified strongly during the reaction. Meanwhile, there were slight mesopore enlargements between the reduced and spent catalysts on Ni-Mg/D-S and Ni-Mg/D-N samples, meaning the internal pores may be modified during the reaction. The mean pore sizes of the catalysts had not changed largely after the reaction. In conclusion, the Ni-Mg/D-N sample possesses the highest SSA, leading to more exposure of active sites.

The X-ray diffraction (XRD) patterns of the catalysts after reduction and test were shown in Fig. 4.1. As shown in the patterns, the small broad diffraction peak at $2\theta=21.5^\circ$ for all samples is attributed to the diffraction of amorphous silica, and the weak peaks at $2\theta=26.7^\circ$ and 28° are assigned to the diffraction of quartz phase, and the three strongest peaks located at $2\theta=44.6^\circ$, 51.9° , 76.5° correspond to the metallic Ni planes of (1 1 1), (2 0 0) and (2 2 0) [301,302]. The particle

sizes of crystalline Ni⁰ were calculated in Table 4.1. It can be seen there is nearly no difference of metallic Ni for reduced or spent catalysts when the nickel salt was changed. After the reaction, the crystal size of Ni⁰ became smaller compared to the reduced catalysts, meaning the redistribution of Ni⁰ during reaction [144].

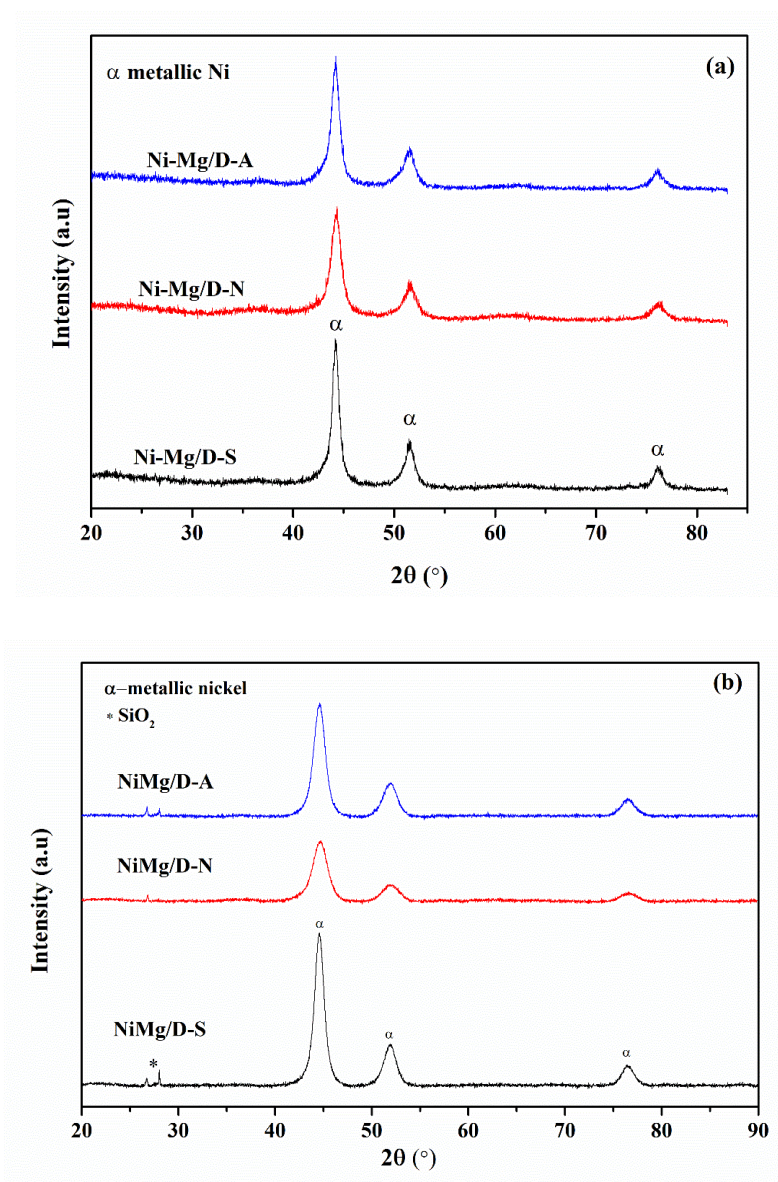


Figure. 4.1. XRD pattern of the reduced (a) and spent (b) catalysts.

4.1.4. Reducibility, basicity distribution of catalysts

The reducibility and basicity of catalysts were measured by H₂-TPR and CO₂-TPD. The profiles are displayed in Fig.4.2a and Fig.4.2b, respectively. Also, the H₂ consumption amount and basic site distribution are calculated in Table 4.2 and Table 4.3. For the TPR-H₂, the curves of all samples can be divided into 3 peaks i.e. α , β , and γ , corresponding to the reduction of small NiO on the surface (Ca.300-400 °C), bulk NiO weakly interacting with the support (Ca.400-500 °C) and nickel silicate or small NiO particles in the pore that are difficult to reduce [303]. As shown in Table 4.2, compared to the Ni-Mg/D-S, temperatures of β and γ peaks for the other samples are higher, indicating stronger Ni-support interaction. The total H₂ consumptions were similar, indicating that the reducible nickel species for the catalysts are similar.

The desorption peaks of CO₂ (Fig.4.2b) can be fitted into three peaks, representing weak, medium, and strong basic sites of the catalyst, respectively [160,258,259,303]. The highest basic sites of weak or medium and lowest strong basic sites (Table 4.3) were observed on NiMg/D-N catalyst. And the medium or weak basic sites of the other two samples are similar.

Table 4.2 H₂ consumption of catalysts calculated according to H₂-TPR

Catalyst	Temperature [°C]			H ₂ consumption [mmolH ₂ /g]			Total [mmolH ₂ /g]
	α	β	γ	α	β	γ	
NiMg/D-S	353	425	520	0.22	1.41	1.44	3.07
NiMg/D-N	369	464	578	0.09	1.02	1.85	2.96
NiMg/D-A	343	479	599	0.14	1.31	1.32	2.77

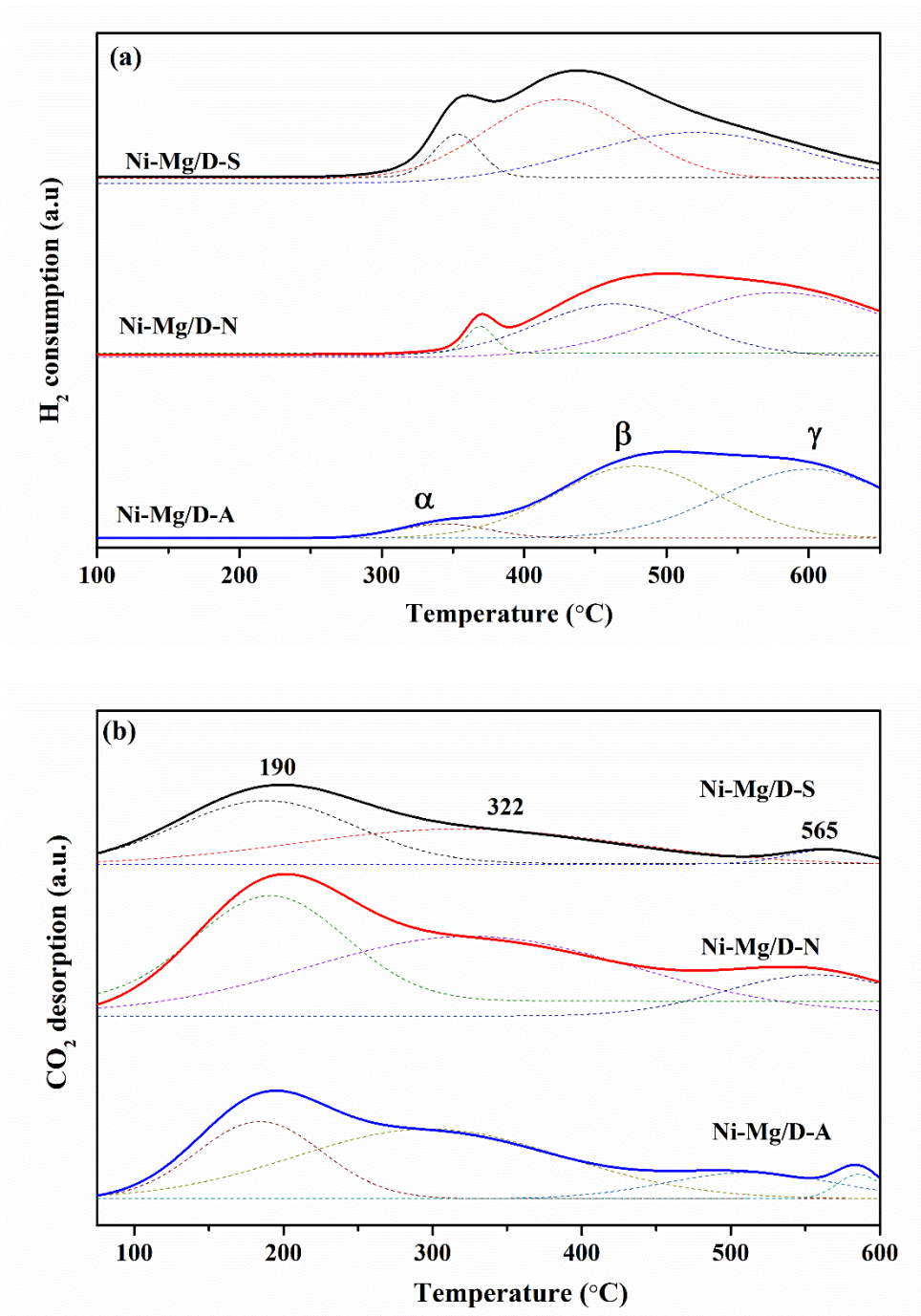


Figure. 4.2. (a) H₂-TPR profiles of fresh catalysts; (b) CO₂-TPD profiles of reduced catalysts;

Table 4.3 Basic site distribution calculated from TPD-CO₂ on reduced catalysts.

Catalyst	Basic sites [$\mu\text{mol/g}$]				Distribution of basic sites [%]		
	Weak	Medium	Strong	Total basicity	Weak	Medium	Strong
NiMg/D-S	30.5	35.5	6.6	72.7	42.0	48.9	9.1
NiMg/D-N	35.6	48.9	9.3	93.8	37.9	52.2	9.9
NiMg/D-A	32.8	36.9	12.1	81.8	40.1	45.0	14.8

4.1.5. Catalytic performance of catalysts for CO₂ methanation

The catalytic activity of catalysts in CO₂ methanation reaction was performed in a tubular U-type quartz reactor under ambient pressure, the temperature of catalyst was monitored by a K-type thermocouple. Before the reaction, the sample (100 mg) was reduced in-situ by the H₂ mixture (5% H₂/Ar, 100 mL/min) at 700 °C with a ramp of 10 °C/min for 1 h. After the reduction, the furnace was cooled down to 250 °C, then the gas mixture (CO₂/H₂/Ar=15/60/25, 100 mL/min, WHSV=60,000 h⁻¹·g_{cat}⁻¹) was fed into the reactor. The products were analyzed in an Agilent Varian 4900 online micro chromatograph. The reaction was conducted from 250 °C to 450 °C with a step of 50 °C with a duration time of 30 min at each temperature. The CO₂ conversion and CH₄ selectivity were calculated based on Equations 1 and 2 in chapter 3, respectively.

The activities of the catalysts are thus presented in Fig.4.3 in which the thick black lines represent the thermodynamic plots of CO₂ conversion and CH₄ selectivity. The CO₂ conversion for all catalysts at the range of 250-300 °C seems very low and it increases with the rising temperature. The CO₂ conversion of Ni-Mg/D-N is higher than that of others at each temperature step. Regarding the CH₄ selectivity, there is no large difference for all catalysts at the range of 250-300 °C. However, the Ni-Mg/D-N sample always possesses the highest selectivity when temperature exceeds 350 °C. Ni-Mg/D-A shows the worst CH₄ selectivity at the running temperature range.

Correlating the medium basic sites of catalysts with the CO₂ conversion values at 350-450 °C, it can be found that the CO₂ conversion increases with the increase of medium basic sites. The crystalline size of Ni⁰ after the test as shown in Table 4.1 decreased compared with that of reduced catalysts, indicating no sintering happened during the reaction. Ni-Mg/D-N shows the best CO₂ conversion and CH₄ selectivity. Thus, it can be deduced that the nitrate nickel salt is the best candidate for diatomite-supported Ni catalysts for CO₂ methanation.

The highest activity of Ni-Mg/D-N catalyst could be attributed to the highest SSA, the small Ni⁰ particle size, the highest medium/total basic sites, and good reducibility. It is reported that the H₂ dissociates on the surface of Ni⁰ and the CO₂ adsorbs and dissociates on the weak or medium basic sites [160]. For Ni-Mg/D-N, the small Ni⁰ particle could provide more active sites for H₂ dissociation, and the high basic sites, especially the medium sites, are beneficial for the adsorption and dissociation of CO₂, thus promote the activity in CO₂ methanation [160].

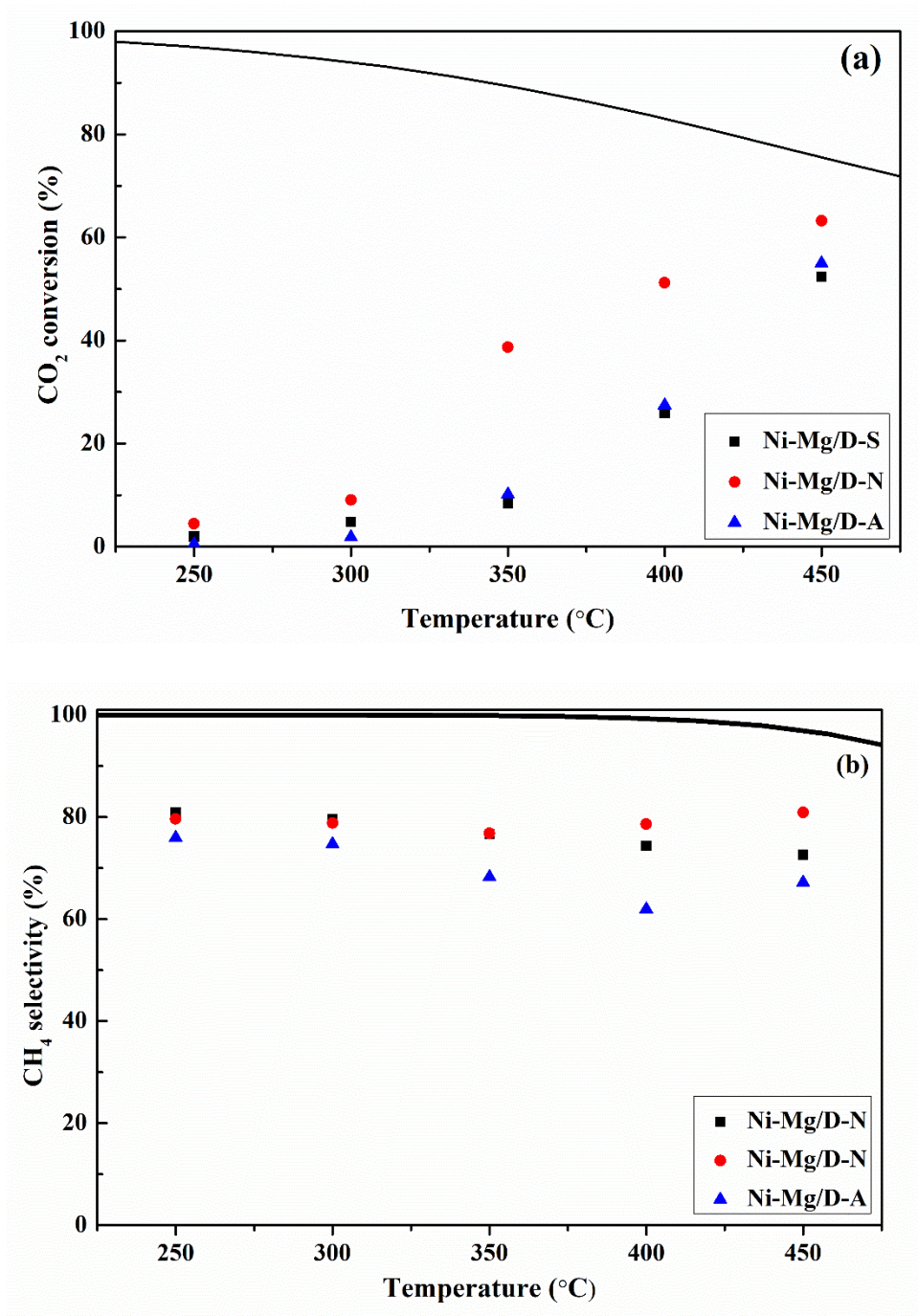


Figure. 4.3. CO₂ methanation results on the catalysts (H₂/CO₂/Ar=60/15/25, WHSV=60,000 h⁻¹g_{cat}⁻¹), (a) CO₂ conversion; (b) CH₄ selectivity

4.1.6 Conclusions of diatomite supported Ni-Mg catalysts

In this study, the Ni-Mg catalysts supported on diatomite were prepared by the precipitation-deposition method with different nickel salts. The effect of nickel salts on the performance of Ni catalysts in CO₂ methanation was investigated by H₂-TPR, CO₂-TPD, N₂ physisorption, and XRD methods. It was found that the Ni-Mg/D-N catalyst presented the best activity and selectivity, which could be ascribed to the small Ni⁰ particle, good reducibility, and the highest medium basic sites.

However, the activity results of diatomite-based Ni catalysts in this chapter seem not satisfactory. The diatomite-supported catalysts in CO₂ methanation still need more development to improve the activity.

4.2 Nickel-based mixed oxides derived from layered-double hydroxide (LDH)

4.2.1 Introduction

Layered double hydroxides (LDH) or hydrotalcite (HT) are materials with di- and tri-valent cations incorporated into the brucite-like layers. The layers of hydrotalcite are positively charged and anions present in the interlayer spaces are compensating the charge. It was reported in the literature that there is a wide range of cations that may be incorporated into the hydrotalcite structure, e.g., Li⁺, Ti⁴⁺, Sn⁴⁺, or Zr⁴⁺ [304]. The calcination of such materials leads to the formation of mixed nano-oxides with periclase-like structures, which show very interesting features [58,63,167,305–307]. Redox or acid-base properties of such materials may be tailored to some extent by controlling hydrotalcite composition, as shown e.g. in NH₃-SCR [308–312] or DRM [44,250,307,313–315] reactions. Another advantage of double-layered hydroxides is that the incorporated cations are usually homogeneously distributed due to their random arrangement in the brucite-like layers. Moreover, such materials exhibit basic properties, which are of great interest when used as catalysts for the reaction of CO₂ methanation [131,138,205,206,208,250,308,316].

Several aspects were already investigated in the case of hydrotalcite-derived catalysts for CO₂ methanation reaction such as (i) the effect of nickel content, (ii) the particle size of nickel crystallites, (iii) the reducibility of nickel species, (iv) the number and distribution of basic sites, and (v) the promotion with other metals such as La, Fe, etc. or the new preparation method [131,138,206,317–320].

Fan et al. [321] studied Ni impregnated MgAl₂O₄ derived from hydrotalcite followed by calcination at 500 °C or treated by DBD plasma to decompose Ni precursor. The plasma treatment resulted in higher nickel dispersion of 7.1% for the plasma decomposition method prepared sample, compared to 6.0% for the traditionally calcined material. The authors claimed that smaller

metallic nickel particles resulted in enhanced activity in the reaction of CO₂ methanation. Wang et al. [319] studied Ni/Al HTs promoted with 0.05 and 0.25% molar ratio of Fe and found that the introduction of Fe effectively enhanced the H₂ adsorption capacity. Ni/Mg/Al hydrotalcite promoted with a wide range of Fe content (1.2-18 wt.% of Fe) were examined by Mebrahtu et al. [237]. It was found that the activity in CO₂ methanation was effectively increased in the low-temperature region when low amounts of iron were introduced. In our previous reports, we investigated the influence of Ni loading and the effect of La introduction on the catalytic activity of LDHs catalysts in CO₂ methanation [131,206,208]. The incorporation of higher amounts of nickel, as well as the introduction of lanthanum, significantly enhanced the activity in CO₂ methanation reaction. This could be correlated with the increased number of medium-strength basic sites, which in the case of La-promoted catalysts was strongly dependent on the method of promoter introduction [131,160,322]. According to the study of Pan et al. [160] CO₂ adsorbed on Ni/Ce_{0.5}Zr_{0.5}O₂ may undergo hydrogenation easier than on Ni/Al₂O₃ because of the higher content of medium basic sites.

Yttrium had been reported in the literature as a promising dopant in methane dry reforming (DRM) reaction ($\text{CO}_2 + \text{CH}_4 = 2\text{H}_2 + 2\text{CO}$) [44,50,51,64,250,316,323,324]. The increased activity of the Ni-containing hydrotalcite was attributed to the enhanced dispersion of the active phase in comparison with the un-promoted materials [51,250,316]. The stability of the Zr- containing catalysts in DRM reaction was also enhanced by the introduction of Y, which was assigned to the formation of a solid-solution ZrO₂-Y₂O₃, leading to the increased reducibility of bulk NiO [44]. Moreover, Bellido et al. [325] reported that ceria doped with yttrium showed enhanced oxygen mobility and oxygen vacancies. For CO₂ methanation, Muroyama et al. [198] reported that Y₂O₃ impregnated with Ni revealed very high activity in the low-temperature region in CO₂ methanation

when compared to Ni supported on Al₂O₃, ZrO₂, and CeO₂ catalysts. It was attributed to the promoted decomposition of formate species formed during the reaction over Ni/Y₂O₃ catalysts.

The purpose of this part is to study yttrium promoted Ni-containing hydrotalcite-derived catalysts for CO₂ hydrogenation to methane. Our study is focused on the determination of the influence of Y introduction to Ni-containing layered double hydroxides on the catalytic performance in CO₂ methanation. The catalysts were synthesized using the co-precipitation method at a constant pH and with a fixed molar ratio of $M^{II+}/M^{III+}=3.0$. The assumed loading of yttrium introduced into hydrotalcite was 0.4, 2.0, and 4.0 wt.%. To correlate the changes in activity with the Physico-chemical properties, the studied materials were characterized using various techniques such as X-ray diffraction (XRD), low-temperature N₂ sorption, X-ray fluorescence (XRF), temperature-programmed reduction in H₂ (H₂-TPR), temperature-programmed desorption of CO₂ (CO₂-TPD), thermogravimetric analysis (TGA) and temperature-programmed oxidation (TPO).

4.2.2 Catalyst preparation

The Layered-double hydrotalcite incorporated with or without yttrium were prepared by the co-precipitation method. The as-synthesized materials were calcined to obtain the mixed nano-oxides. The particular preparation process was described in 3.1.2 of Chapter 3. The samples were denoted as MO-0Y, MO-0.4Y, MO-2.0Y, and MO-4.0Y. The Characterization techniques used in this chapter are detailed in chapter 3.

4.2.3 Structural parameters, elemental composition, and textural properties of nano-mixed oxides derived from hydrotalcite

Structural parameters calculated from the XRD diffractograms acquired for as-synthesized materials are reported in Table 4.4. The structural parameters a and c were obtained by the equations of $a=2d_{(110)}$ and $c=d_{(003)}+2d_{(006)}+3d_{(009)}$. The crystallographic parameter a ($2d_{(110)}$) is associated with the average cation-cation distance in the hydroxide layers [63]. The parameter a is stable for all materials (3.06 Å), indicating the lack of possible distortions of the lattice. As stated by García-García et al. [326], yttrium can be incorporated into layers of double-layered hydroxides, though its ionic radius is somewhat larger than that of Al and Mg ($Mg^{3+}=0.86$ Å, $Al^{3+}=0.675$ Å, $Y^{3+}=1.04$ Å) [250,327]. The obtained parameter c ($d_{003} + 2d_{006} + 3d_{009}$), which refers to the triple thickness between brucite layers in hydrotalcite structure, decreased for low Y (under 2 wt.%) modified samples in comparison to the non-modified material, except for MO-4.0Y, which increased to 23.51 Å (Table 4.4). For the MO-4.0Y, some deposition of Yttrium on the external surface may be assumed. Moreover, the distance between the brucite-like layers ($c'=c/3$) is in the range of 7.79-7.84 Å, showing the presence of interlayer anions, such as e.g. CO_3^{2-} (7.65 Å) and NO_3^- (8.79 Å) [304,328,329]. The structural parameters revealed that the yttrium loading up to 2.0 wt.% could result in the introduction of this metal into the periclase-like structure. However, the higher content of the yttrium led to the increase of the interlayer space, which was possibly linked with the deposition of the metal on the surface of the layers. This agrees with the textural properties, as the specific surface area of MO-4.0Y significantly decreased compared with that of MO-2.0Y due to their partial blockage.

The elemental composition of nano-mixed oxides obtained by calcination acquired from the XRF method is presented in Table 4.4. All samples revealed nickel content between 16 and 20 wt.%, whereas the content of yttrium was either the same (MO-0.4Y) or close to the nominal amount (MO-2.0Y and MO-4.0Y). According to Li et al. [64], Ni^{2+} can be substituted by Y^{3+} , similarly as

observed in our study (Table 4.4). The calculated M^{2+}/M^{3+} atomic ratios were fairly close to those assumed during the materials synthesis, indicating that the composition of LDHs may be easily controlled as reported before [62].

Table 4.4 Structural parameters (XRD), elemental composition (XRF), and textural properties (BET analysis) of yttrium modified nano-mixed oxides derived from hydrotalcite. Additionally, the nominal values are reported in brackets.

Catalyst	Structural parameters		Elemental composition of the calcined materials			Textural properties of the calcined materials		
	a	c	Ni [wt.%]	Y [wt.%]	M^{2+}/M^{3+} [-]	S_{BET}	V_p	d_p
	[Å] ^{a)}	[Å] ^{b)}				[m ² /g] ^{c)}	[cm ³ /g] ^{d)}	[nm] ^{e)}
MO-0Y	3.06	23.45	20	-	3.6 (3.0)	120	0.6	19
MO-0.4Y	3.06	23.38	21	0.4 (0.4)	3.5 (3.0)	120	0.5	15
MO-2.0Y	3.06	23.42	18	1.8 (2.0)	3.4 (3.0)	192	0.6	14
MO-4.0Y	3.06	23.51	16	3.4 (4.0)	3.7 (3.0)	153	0.7	18

^{a)} calculated from d-spacing of (110) plane; $a = 2d_{110}$

^{b)} calculated from appropriate d-spacings of (003), (006) and (009) planes; $c = d_{003} + 2d_{006} + 3d_{009}$

^{c)} specific surface areas calculated from the BET equation

^{d)} mesopore volumes obtained from the BJH desorption calculation method

^{e)} pore size distribution derived from the BJH desorption calculation method

The textural parameters obtained from the N₂ sorption isotherms for the calcined materials are listed in Table 4.4. All values agree with those previously reported in the literature [44,51,131,138,208,250,304,308,316,322]. The obtained specific surface areas ranged between 120 and 192 m².g⁻¹ and the highest area was found for the MO-2.0Y catalyst. There are no significant differences regarding BET surface area and pore volume of Ni-containing double-layered hydroxides-derived catalyst when the loading of yttrium is low ($\leq 0.4\%$) compared with Y-free sample, only the average pore size decreases as the increase of yttrium at a low loading of

yttrium [250,316]. As described in the section before, the structural parameters showed that the yttrium loading up to 2.0 wt.% could result in the introduction of this metal into the periclase-like structure. However, the higher content of the yttrium increased the interlayer space, which was possibly linked with the deposition of the metal on the outer surface of the layers. This agrees with the textural properties, as the specific surface area of MO-4.0 Y significantly decreased due to their partial blockage. The volume of mesopores did not change significantly after yttrium promotion. However, pore diameters diminished for MO-0.4Y and MO-2.0Y catalysts, as compared to the non-promoted material, pointing to the formation of a higher number of smaller pores when yttrium was introduced into the brucite-like layers.

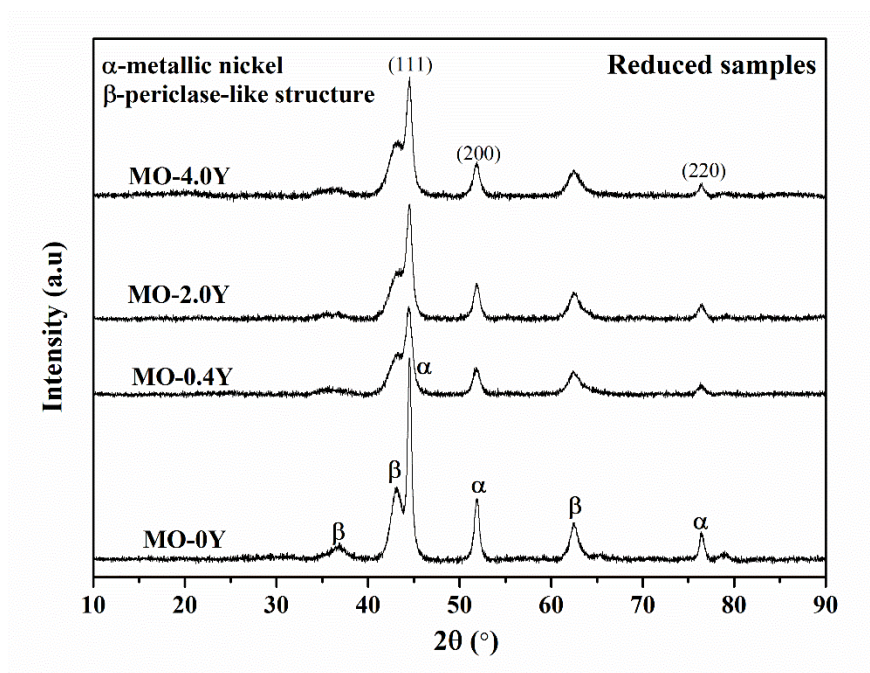


Figure. 4.4. XRD profiles for reduced nano-mixed oxides modified with different yttrium loadings (0.4, 2.0, or 4.0 wt.%) and compared to the un-promoted catalyst (MO-0Y).

Fig.4.4 shows XRD diffractograms of the reduced catalysts, in which metallic nickel phase (ICOD 01-087-0712) is evidenced by the presence of reflections at 2θ ca. 44.5, 53 and 76.5°, corresponding to crystal planes of (111), (200) and (220), respectively. Moreover, reflections arising from the periclase-like structure at 2θ ca. 36.7, 43 and 62.5° are observed, which corresponds to mixed oxides obtained after thermal treatment of double-layered hydroxides [44,250,316]. Table 4.5 reports the size of Ni⁰ crystallites, calculated from the 2θ diffraction peak at ca. 52° (corresponding to (200) crystal plane of Ni⁰) using the Scherrer equation. The yttrium promotion resulted in a decrease of nickel crystallites size from ca. 13.7 nm for the parent MO to ca. 9.2 nm for MO-0.4Y. The values obtained for MO-2.0Y and MO-4.0Y catalysts were close to the one registered for the un-promoted catalyst, i.e. 12.5 and 12.3 nm, respectively.

Table 4.5 Ni⁰ crystallite size for the reduced and spent materials calculated from XRD

Catalyst	Ni ⁰ crystallite size	
	Reduced samples [nm] ^{a)}	Spent samples [nm] ^{a)}
MO-0Y	13.7	9.3
MO-0.4Y	9.2	7.9
MO-2.0Y	12.5	7.6
MO-4.0Y	12.3	7.5

^{a)} Calculated from the Scherrer equation at $2\theta = 52^\circ$

4.2.4 Reducibility of catalysts followed by H₂-TPR

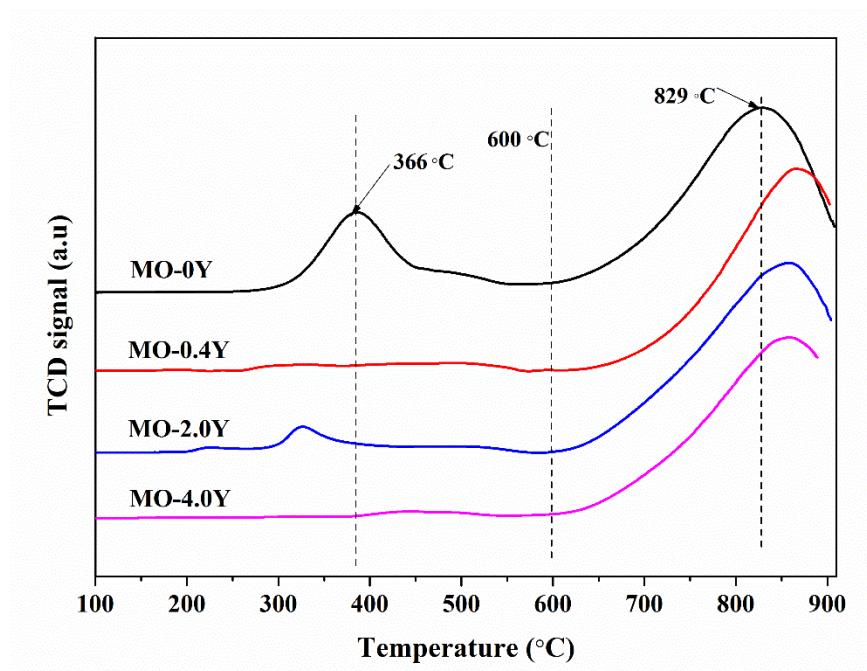


Figure. 4.5. H₂-TPR profiles for mixed oxides modified with different yttrium loadings (0.4, 2.0, or 4.0 wt.%) compared to the non-promoted catalyst (MO-0Y).

Fig.4.5 shows the H₂-TPR of calcined mixed oxides (MO). As demonstrated in other reports, the yttrium cannot be reduced under the conditions used in the measurements [64,325]. The reduction profile of MO-0Y has two main reduction bands that centered at 366 °C and 829 °C, which corresponds respectively to the reduction of nickel oxides weakly bonded with the double-layered hydroxides and nickel species that are incorporated into the structure of hydroxides [50,58,64,250,325,330]. The high-temperature peak shifts towards higher temperatures for all Y-promoted catalysts (Table 4.6, 858-866 °C), which indicates stronger interaction between nickel oxide species and the support matrix in comparison with the Y-free sample [250]. For 2.0 and 4.0 wt.% of Y, the shift of the latter peak was less pronounced, as shown in Table 4.6, indicating less strong metal-support interaction. This might be due to the segregation of yttrium or lattice

substitution of nickel species by yttrium [64]. The reduction peaks at temperatures lower than 600 °C presented low intensity for Y-modified samples in comparison to the un-promoted catalyst (MO-0Y), which means that the loading of Y results in a decreased reducibility. This phenomenon was already observed in hydrotalcite derived mixed oxides catalysts modified by Y and Zr in CO₂ dry reforming reaction, in which the adding of Y and Zr resulted in a decrease of the reducibility of nickel [58,250]. As calculated in Table 4.6, the highest H₂ consumption (1.67 mmol) was obtained for the Y-free mixed-oxide sample. After the introduction of yttrium, the H₂ consumptions (1.15-1.38 mmol) of yttrium-promoted mixed oxides decreased in contrast to the yttrium-free sample, demonstrating decreased reducibility of NiO for yttrium-promoted mixed oxides.

Table 4.6 H₂ consumption according to H₂-TPR analyses

Catalyst	Temperature (°C)		H ₂ consumption (mmolH ₂ /g)		
	<600	>600	<600	>600	Total
MO-0Y	386	829	0.37	1.30	1.67
MO-0.4Y	320	866	0.07	1.09	1.16
MO-2.0Y	327	858	0.11	1.27	1.38
MO-4.0Y	444	858	0.05	1.10	1.15

4.2.5 Basicity of the catalysts derived from CO₂-TPD

Fig.4.6 shows the CO₂-TPD profiles of the reduced MO catalysts. Three types of CO₂ desorption peaks could be observed with a maximum temperature of 138, 203, and 364 °C for the MO-0Y sample, which refers to weak, medium (intermediate), and strong basic sites, respectively [63,138,250,307]. Similar peaks were found for yttrium-promoted mixed oxides materials, with the maximum temperature of CO₂ desorption peak shifted towards lower temperature with the

increasing yttrium content compared to the MO-0Y sample, indicating that the loading of Y changed the number and distribution of the basic sites. This phenomenon was also observed in other literature [250].

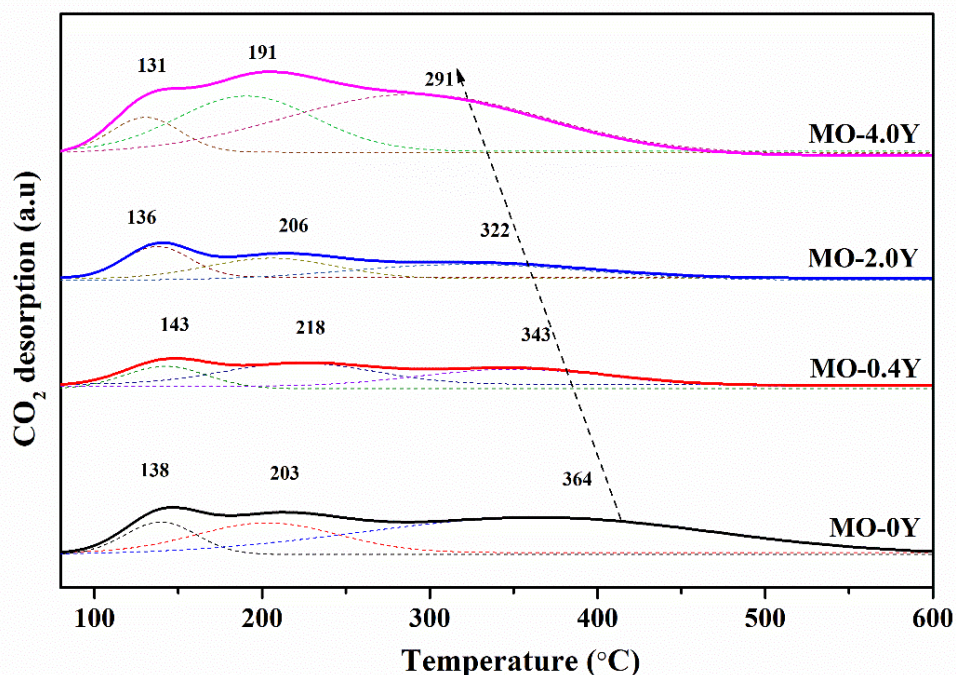


Figure. 4.6. CO₂-TPD profiles for mixed oxides catalysts

As calculated in Table 4.7, the amount of different type of basic sites for the Y-modified samples increased with the increase of yttrium loading (from 0.4 to 4.0 wt%) and the total number of basic sites also increased with the increased Y content, with MO-4.0Y having the highest number of each type of basic sites as well as the total basic sites. Compared to the basicity of the MO-0Y sample, the materials with 0.4 wt.% and 2.0 wt.% of Y showed lower content of total basic sites and individual types of basic sites (weak, medium, or strong). But compared to that of the MO-0Y, the percentage share of weak or intermediate basic sites for MO-0.4Y and MO-2.0Y was higher, with lower content of the share of strong basic sites, meaning that the doping of yttrium

significantly changed the distribution of basic sites on Y-modified samples. In conclusion, the introduction of Y with low content (0.4 wt.% and 2.0 wt.%) increases the share of medium basic sites at the expense of strong type. The highest share of medium-strength basic sites was found on the MO-0.4Y sample.

Table 4.7 Basicity of the studied catalysts, calculated from TPD-CO₂ for the reduced materials.

Catalyst	Basic sites [$\mu\text{mol/g}$]				Basic sites distribution [%]		
	Weak	Medium	Strong	Total basicity	Weak	Medium	Strong
MO-0Y	16.4	43.9	46.3	106.6	15.4	41.2	43.4
MO-0.4Y	9.4	33.7	14.6	57.7	16.2	58.5	25.3
MO-2.0Y	11.6	35.2	26.4	73.2	15.8	48.1	36.1
MO-4.0Y	41.4	91.5	91.2	224.1	18.5	40.8	40.7

4.2.6 Catalytic performance tests for CO₂ methanation

The catalytic tests of CO₂ methanation were performed in the same reactor presented above. Prior to the catalytic tests, the calcined materials were reduced in situ from room temperature to 900 °C with a heating rate of 5 °C/min under reduction gas (5% H₂/Ar: 100 ml/min) and kept 1 h at 900 °C. The reduction temperature was 900 °C because the nickel species could be reduced thoroughly at 900 °C according to the TPR result, which was also used in other literature [131]. After the reduction, the reactor was cooled down to 200 °C and the reaction mixture was introduced with a molar ratio of Ar/H₂/CO₂=25/60/15 and the GHSV of 12,000 h⁻¹. Subsequently, the methanation tests were performed in the temperature range from 200 to 400 °C with a temperature step of 50 °C, which are appropriate conditions for Ni-containing mixed oxides, as reported in many works

[131,322]. At each plateau of temperature, the catalyst was kept for 30 min, corresponding to a steady-state measurement. The flow rates of inlet and outlet were measured by flowmeter at each temperature when the reaction was stable (after 30-45 minutes of reaction). And the measured flow rates and the compositions obtained from GC were used to calculate the CO₂ conversion (X_{CO_2}) and CH₄ selectivity (S_{CH_4}) as reported in Chapter 3.

Fig. 4.7 presents the CO₂ conversion and Fig.4.8 presents the methane selectivity measured during catalytic experiments for the studied mixed oxides (MO) promoted with different amounts of Y as a function of reaction temperature.

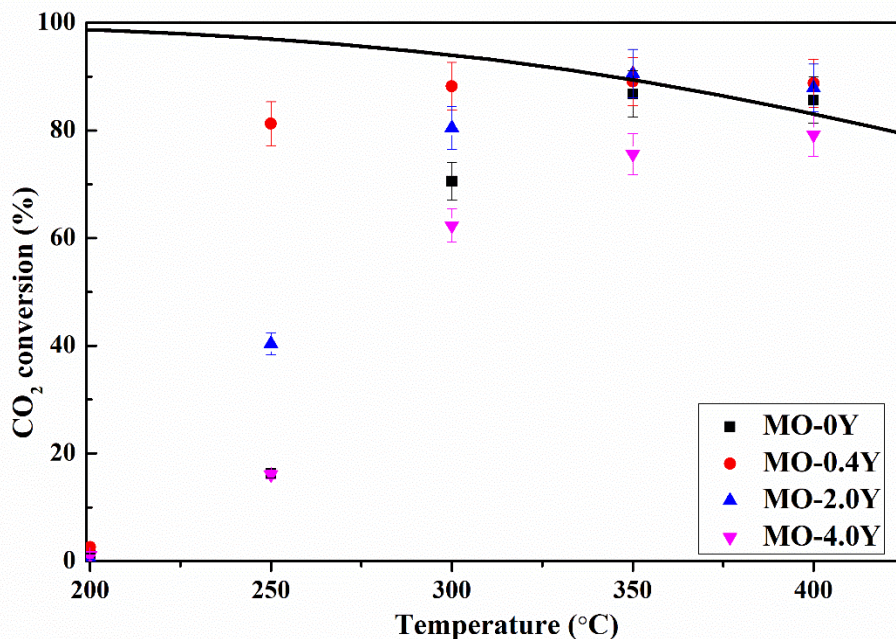


Figure. 4.7. CO₂ conversion of the studied mixed oxides catalysts (MO-0Y, MO-0.4Y, MO-2.0Y, MO-4.0Y).

Experimental conditions of CO₂ methanation: GHSV=12000 h⁻¹, total flow 100 mL/min, CO₂/H₂/Ar =15/60/25.

The thick continuous line shown in Fig.4.7 represents the thermodynamic equilibrium calculated for the conditions used in this work [63,138]. According to thermodynamics, CO₂ methanation is favored at low temperatures and it decreases with the increasing temperature due to the co-

existence of parallel reactions, such as reverse water-gas shift (RWGS) or reforming [63,331]. The latter results in undesired side products, among them carbon monoxide [322]. All mixed oxides were catalytically active in CO₂ methanation. The obtained conversions at 250 °C were much lower than the thermodynamic limitations, except for the MO-0.4Y catalyst. Depending on the Y-loading a change in the catalytic performance of the catalysts was observed. Nevertheless, the increase of the catalytic activity was not directly correlated to the increase of yttrium loading. For both series of results registered at 250 °C and 300 °C, the sequence for the CO₂ conversion was: MO-0.4Y > MO-2.0Y > MO-0Y > MO-4.0Y. CO₂ conversion increased at 250 °C from 16% for MO-0Y to 40% and 81% for MO-2.0Y and MO-0.4Y, respectively, and at 300°C, from 71% for MO-0Y to 80% and 88% for MO-2.0Y and MO-0.4Y, respectively. At both temperatures, 250 °C, and 300 °C, the selectivity towards methane was higher than 98.5%, with very low differences between the Y-promoted catalysts (Fig.4.8). However, in the tested temperature range, both the CO₂ conversion and CH₄ selectivity for MO-4.0Y decreased in comparison to MO-0Y. This could have been caused by the deposition of the yttrium on the external surface of the support matrix and the weaker metal-support interaction, as confirmed by XRD and TPR-H₂.

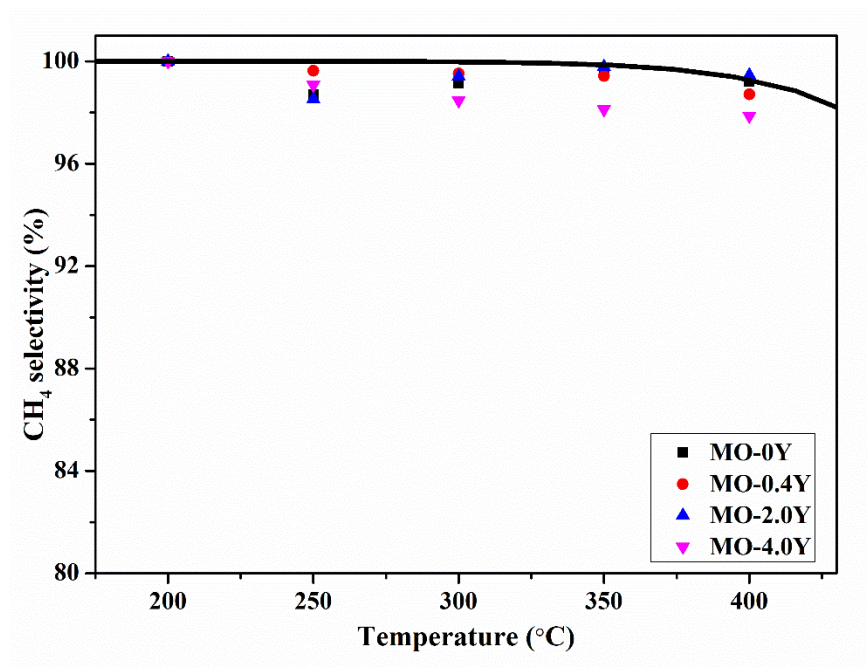


Figure. 4.8. CH₄ selectivity of the studied mixed oxides catalysts (MO-0Y, MO-0.4Y, MO-2.0Y, MO-4.0Y).

Experimental conditions of CO₂ methanation: GHSV = 12000 h⁻¹, total flow 100 ml/min, CO₂/H₂/Ar = 15/60/25.

The enhancement of the activity of Y-promoted catalysts except MO-4.0Y can be partially explained by the smaller Ni⁰ crystallite size in comparison to the non-promoted sample, which is also found for La-promoted Ni-containing hydrotalcite-derived mixed oxides in CO₂ methanation [206].

Simultaneously, the MO-0.4Y catalyst showed the highest percentage share of intermediate-strength basic sites. Pan et al. [332] claimed that Lewis acid-base sites are involved in the CO₂ methanation mechanism and the CO₂ adsorbed on strong basic sites did not participate in the reaction and the medium-strength basic sites played an important role in the reaction. In the current study, a linear correlation between CO₂ conversion and the percentage share of medium-strength basic sites can be drawn at 250 °C and 300 °C (Fig.4.9). It shows that the CO₂ conversion increase as the increase of the percentage share of medium-strength basic sites.

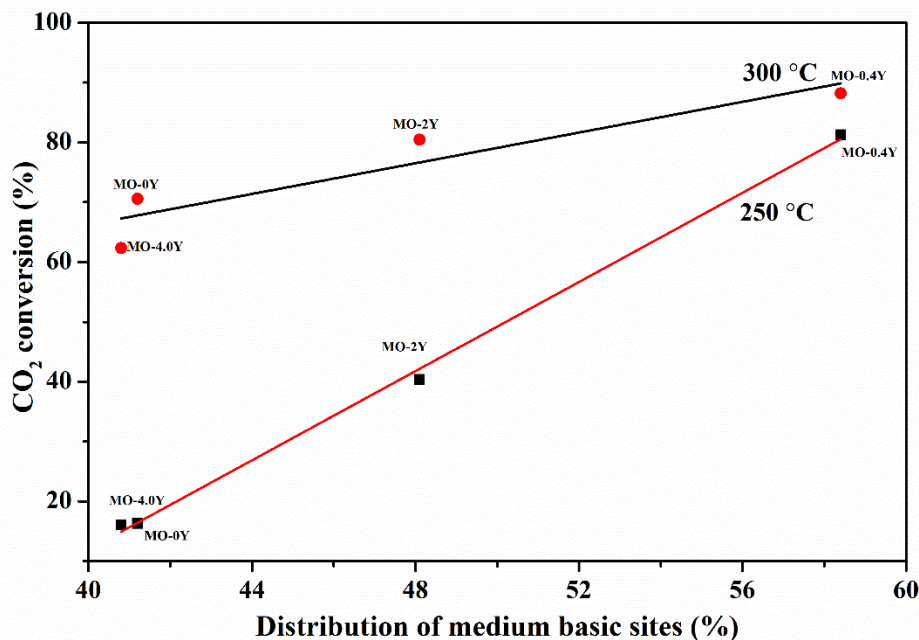


Figure. 4.9. CO₂ conversion at 250 °C and 300 °C versus percentage share of medium basic sites of tested catalysts, the black points represent CO₂ conversion at 250 °C and the red points represent CO₂ conversion at 300 °C

The medium-strength basic sites play a significant role in the methanation process. Wierzbicki et al. [131,322] found that there was a good linear correlation between the number of medium-strength basic sites and the CO₂ conversion on the unpromoted and La-promoted LDHs catalysts. This work confirms that the percentage of medium-strength basic sites has a considerable influence in the case of carbon dioxide methanation on Ni-containing Y-modified mixed oxides catalysts. Besides, the TPR results show that MO-0.4Y has the highest intensity of metal-support interaction compared to that of other samples [333]. In conclusion, the decreased nickel particle size, increased share of medium-strength basic sites, and stronger metal-support interactions found for MO-0.4Y catalyst greatly contributed to the enhanced catalytic activity in CO₂ methanation.

4.2.7 On the evolution of spent samples

4.2.7.1. Structural Evolution

Ni⁰ crystallite sizes calculated for the spent catalysts are reported in Table 4.5. A decrease in the crystallite size was found for the spent catalysts compared to that of the reduced samples, in agreement with Świrk et al. [250] and Dębek et al. [58] on similar materials for other CO₂ reactions. This can be explained by the loss of crystallinity of the Ni phase due to its possible re-dispersion of nickel particles. The decreased crystallite size of Ni⁰ species also indicates that no sintering happened during the reaction.

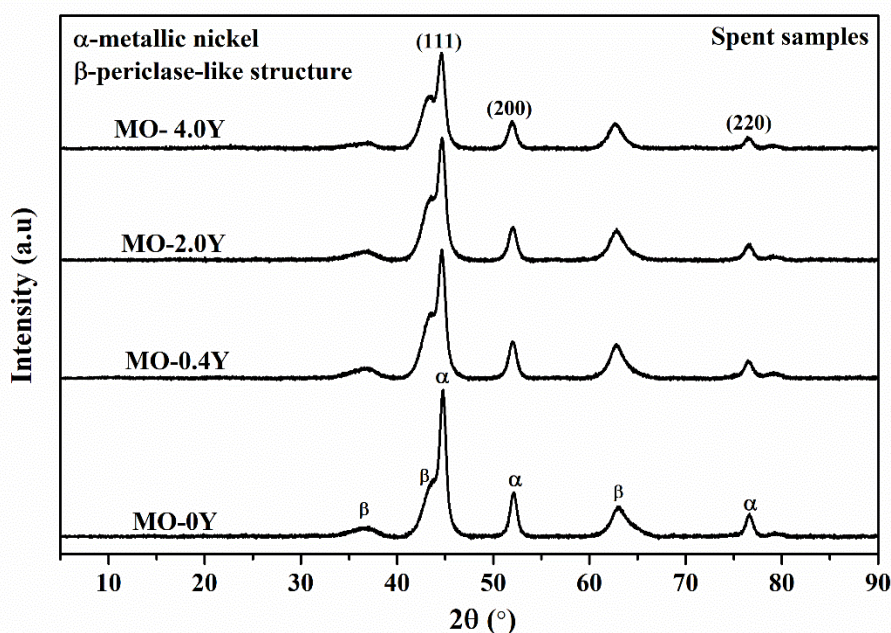


Figure. 4.10. XRD diffractograms of spent Y modified mixed oxides (0.4, 2.0, or 4.0 wt.%) as compared to the unpromoted catalyst (MO-0Y).

After the methanation tests, no reflections corresponding to graphitic carbon (at $2\theta=27^\circ$) were observed in the diffractograms of the spent catalysts (Fig.4.10). Thus, extensive coking with

graphite formation may be excluded. This is in agreement with the studies of other authors e.g. Wierzbicki et al. [131], who confirmed the absence of carbon deposition on Ni/Al LDHs-like catalysts for CO₂ methanation.

4.2.7.2. Surface evolution

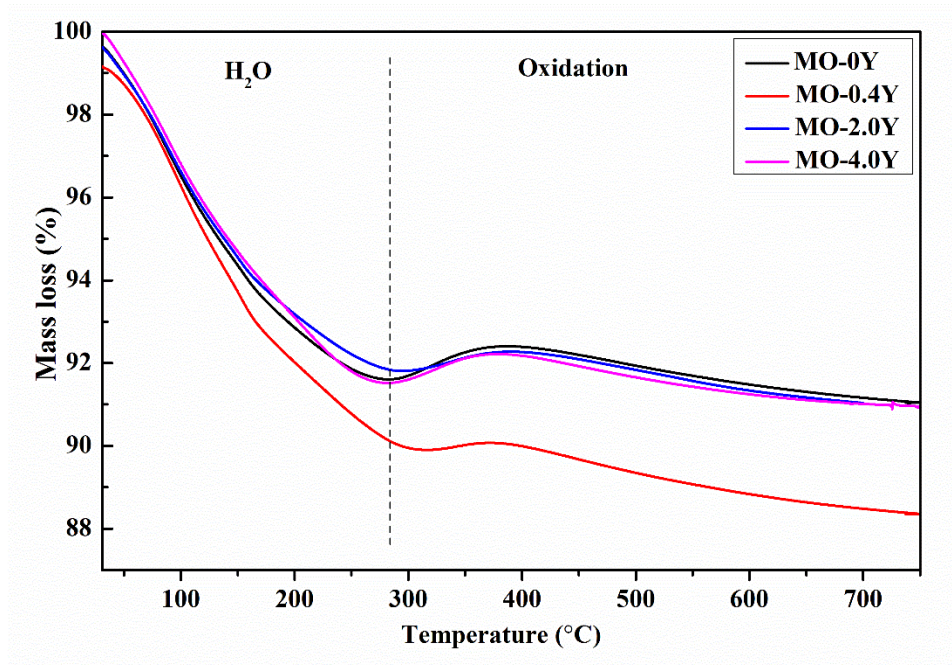
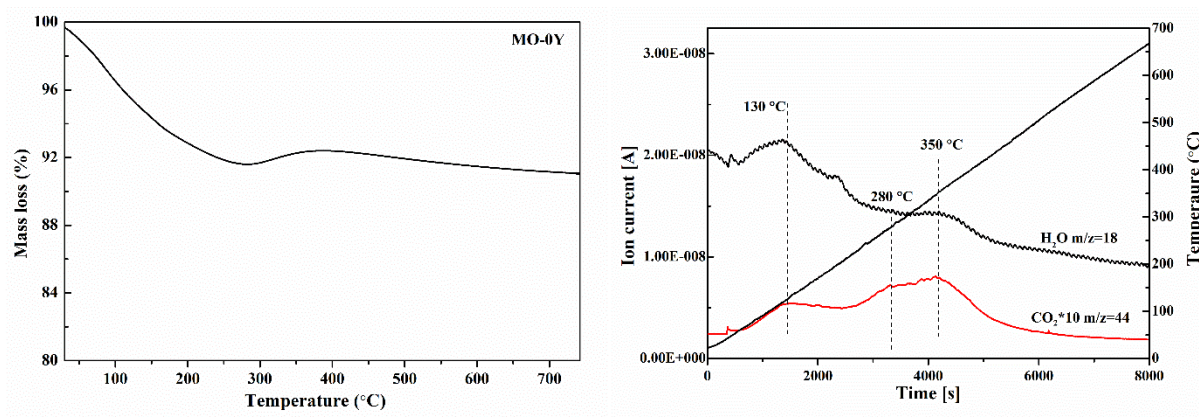


Figure. 4.11. TGA plots of the studied catalysts (MO-Y0, MO-Y0.4, MO-Y2.0, MO-Y4.0) were tested in the methanation process.

Thermogravimetric analyses were carried out for the spent catalysts to verify if other non-crystalline carbon species may have been formed (Fig.4.11). From Fig.4.11, two mass loss regions can be observed for all tested MO samples, corresponding respectively to the removal of physically adsorbed water (<250°C) and a higher temperature region (>400°C) corresponding to oxidation of metallic nickel to nickel oxide and the removal of residues. From TGA, one can conclude that no significant amount of carbonaceous species was present on the surface of the spent catalysts. To

confirm this, temperature-programmed oxidation tests were performed from RT to 650 °C on MO-0Y (Fig. 4.12a) and MO-0.4Y catalysts (Fig. 4.12b).

(a)



(b)

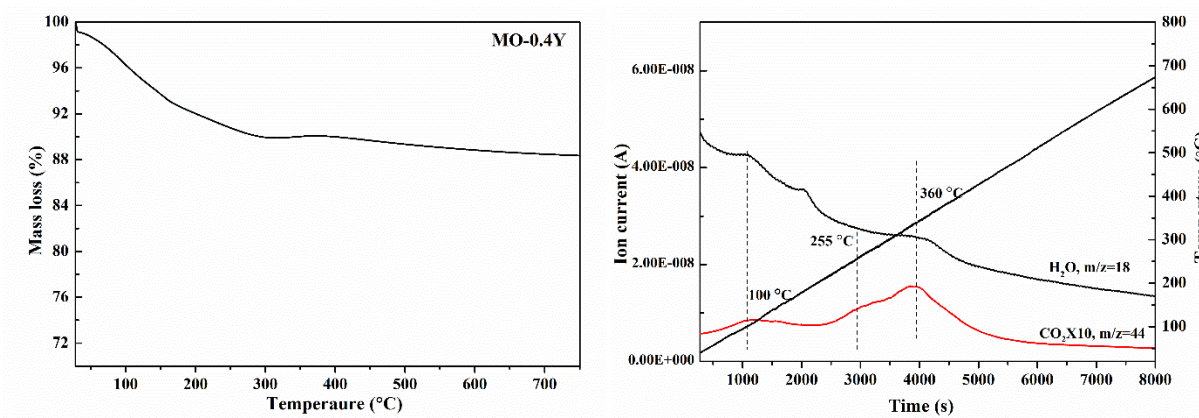


Figure. 4.12. Temperature-Programmed Oxidation results followed by mass spectroscopy (H₂O $m/z=18$ and CO₂ $m/z=44 \times 10$) on catalysts; a) unpromoted MO catalysts, b) MO-0.4Y.

From Fig.4.12a and b, one can observe that CO₂ formation corresponding to the decomposition of carbonaceous species (250-500°C) is very low, confirming insignificant amounts of the formed

carbonaceous species during the CO₂ methanation reaction on the Y promoted catalysts. Thus, the main byproduct of the reaction is CO.

4.2.8 Conclusions of mixed oxides from LDHs

Yttrium-promoted Ni/Mg/Al hydrotalcite-derived catalysts were synthesized using the co-precipitation method at constant pH. Then, the catalysts were characterized by low-temperature N₂ sorption, X-ray diffraction, elemental analysis, and temperature-programmed reduction/desorption (H₂-TPR and CO₂-TPD), and tested as catalysts in CO₂ methanation at GHSV = 12000 h⁻¹ using a mixture of CO₂/H₂/Ar = 15/60/25.

The addition of Y affected the CO₂ adsorption capacity of the materials by changing the distribution of the basic sites, especially those of medium strength. As proven by H₂-TPR, the yttrium promotion influenced the nickel/support interaction. After the introduction of yttrium, a shift of reduction peak towards higher temperatures was observed, which was attributed to the segregation of Y on the support. The Y addition affected strongly the catalytic activity in CO₂ methanation, increasing the CO₂ conversion at 250 °C from 16% for MO-0Y to 40 and 81% for MO-2.0Y and MO-0.4Y, respectively. This could be explained by both increased distribution of medium-strength basic sites and significantly smaller metallic nickel particle size of Y-promoted catalysts. Additionally, the metallic nickel crystallite size decreased after the reaction, which points to the reorganization of Ni at the surface of the support, which could contribute to the increase of the catalytic activity in the moderate temperature region. The selectivity towards methane formation was found around 98 to 99% at 250°C. It is worth noting that the only products of the reaction registered were H₂O, CH₄, and CO. The XRD, TGA, and TPO analyses confirmed only traces of carbon in the spent catalysts.

The mixed oxides Ni catalysts derived from LDHs showed high activity and selectivity in CO₂ methanation. The yttrium promoter showed high improved performance for mixed oxides Ni catalysts.

4.3. Conclusions and perspectives

Ni catalysts based on CeO₂, ZrO₂, and MOF, etc. materials showed high activity and selectivity towards CO₂ methanation [136,212,334]. However, such materials still have a high cost for large-scale applications. The development of Ni catalysts based on low-cost materials or natural materials such as clays, ashes, and bentonite, etc. can help reduce the cost, which has received intensive attention [239,335–340].

In this chapter, the diatomite-supported Ni catalysts and yttrium-promoted Ni/Mg/Al hydrotalcite-derived catalysts were developed to catalyze the CO₂ methanation reaction. Although the diatomite-supported Ni catalysts did not show high performance, they can be improved further by other methods, which will be studied in the future. Their promotion by elements such as La, Y, and Fe would be interesting in a future study.

Ni-based hydrotalcite-derived catalysts are already known to be efficient catalysts for CO₂ methanation reaction. Promotion by Fe and La had shown interesting properties, however, the promotion by Y was never studied before. Herein, it was demonstrated that yttrium-promoted Ni/Mg/Al hydrotalcite-derived catalysts showed high performance at low temperatures during the reaction, indicating a high potential towards commercialization. Thus, the purpose of the next chapter is to use CeO₂ and Y₂O₃ as supports for methanation reaction.



Chapter V

Ni/CeO₂ nanoparticles promoted by yttrium doping as catalysts for CO₂ methanation

5. Ni/CeO₂ nanoparticles promoted by yttrium doping as catalysts for CO₂ methanation

5.1 Introduction

It is well known that noble metal-based catalysts perform good low-temperature activity and selectivity in CO₂ methanation [106]. However, the high cost and low availability make them unappropriated towards application. In such a case, Ni catalysts supported on various oxides become good alternatives for methanation reaction thanks to their benefits of relatively high catalytic activity, low cost, and high availability [187]. Supports with high surface area, appropriate basicity, and strong metal-support interaction, play important roles in enhancing CO₂ conversion and selectivity towards CH₄. Various supports have already been studied for nickel-based catalysts, such as SiO₂ [341], diatomite [143], α -Al₂O₃ [342], ZrO₂ [343], hydrotalcite derived mixed oxides [131,138,206,208], MgO [344], TiO₂ [345], mesoporous oxides [171,346–348], CeO₂, and Y₂O₃ [194,197,210,349,350]. As presented in chapter 4, low-cost materials like diatomite and hydrotalcite-derived mixed oxides were introduced.

In the meantime, CeO₂ had attracted plenty of interest because of its unique redox property. It can create oxygen vacancies during the redox process Ce (III)/Ce (IV), promoting the activation of CO₂ [351]. Tada et al. [170] reported that Ni/CeO₂ catalysts showed higher CO₂ conversion and CH₄ selectivity at low temperatures compared to Ni catalysts supported on α -Al₂O₃, TiO₂, and MgO. Such effect was attributed to the formation of oxygen vacancies on the surface of partially reduced CeO₂, promoting the activation of CO₂ and adsorption of CO₂ derivatives. Zhou et al. [192] prepared CeO₂ with different structures and used the synthesized CeO₂ as support to prepare

Ni/CeO₂ catalysts. The characterization data and CO₂ methanation results revealed that the Ni/CeO₂ catalyst with a well-ordered mesoporous structure had high specific surface area, strong metal-support interaction, smaller Ni⁰ particle size, and higher dispersion of active species than Ni over other ceria oxides, thus showing the highest CO₂ conversion and the best stability at T > 260°C. The study of the CO₂ methanation mechanism over Ni/CeO₂ and Ni/Al₂O₃ catalysts revealed that the high methanation activity and selectivity of Ni/CeO₂ were attributed to the presence at the nickel-ceria interface of active sites for CO₂ dissociation, while dispersed metallic Ni particles activated H₂ [159]. Thus, Ni/CeO₂ based catalysts able to chemisorb and dissociate CO₂ have been widely investigated.

Although several reports claim Ni/CeO₂ as a potential good catalyst for methanation, the catalytic stability with time on stream is still a brake to its industrialization due to the occurrence of side reactions. Many efforts have been devoted to promoting the activity and stability of Ni/CeO₂ catalysts e.g., tailoring the structure of CeO₂, promoting the dispersion of nickel species, increasing the metal-support interaction [139]. Yu et al. [350] added in the preparation of Ni/CeO₂ nanoparticles g-C₃N₄ as a sacrificial and protective template. Several characterization methods used to investigate such catalysts revealed enhanced interaction between Ni and CeO₂ and decreased Ni particle size on the modified catalyst, thus facilitating the adsorption and dissociation of the reactants with higher methanation activity and CH₄ selectivity.

Bian et al. [196] prepared Ni/CeO₂ catalysts with tunable CeO₂ structure i.e. ceria nanorods (NR) and ceria nanocubes (NC) and investigated their catalytic performance in CO₂ methanation. Among the prepared catalysts, the Ni/CeO₂ (NR) exhibited higher conversion and selectivity towards CH₄ at low temperature, which was attributed to the higher concentration of Ce (III) on the surface.

Yttrium has been reported to be an effective promoter of nickel catalysts on double-layered hydroxides for CO₂ methane reforming, because it enhances the redox properties of nickel, increases the specific surface area, and promotes weak and medium basic sites in comparison with non-modified samples [144,250].

Moreover, yttrium has been proven to stabilize ZrO₂ at high temperatures [352]. Kesavan et al. [353] reported Ni/YSZ (Yttrium stabilized ZrO₂) catalysts prepared by different methods for CO₂ methanation and found that the Ni/YSZ synthesized by wet impregnation with EDTA complex showed remarkable stability on time on stream, without deactivation under high CO₂/H₂ ratio. To the best of our knowledge, until now, almost no research concerning the effect of yttrium on Ni/CeO₂ catalysts for CO₂ methanation has been reported.

In this chapter, Ni catalysts supported on yttrium-modified CeO₂ prepared by the hydrothermal method were studied in CO₂ methanation. The present work aims to investigate the relationship between the modification induced by yttrium promotion on the physicochemical properties and catalytic performances of Ni/CeO₂ catalysts. For this purpose, the catalysts as calcined, reduced, or spent (after methanation test or steady-state test) samples were characterized by XRF, XRD, TEM/HRTEM, EDX, H₂-TPR, CO₂-TPD, N₂ adsorption-desorption, XPS, and TGA techniques. The structure-activity relation was discussed.

5.2 Catalyst preparation and physicochemical techniques

The CeO₂ nanoparticles and Ni/CeO₂ nanoparticle catalysts were prepared by the hydrothermal method and wet impregnation method, respectively. The detailed processes were listed in 3.1.3 of

Chapter 3. The names of catalysts were designed as 5Ni/CeO₂, 5Ni/Y₂O₃, and 5Ni/CeO₂-Y_x (Y content, wt.%), respectively.

Elemental analysis of the catalysts was carried out using an X-ray fluorescence wave-dispersive spectrometer (XRF 1800 Shimadzu). According to XRF analyses, the real loading of Ni and Y in the prepared catalysts was equal to the nominal one $\pm 10\%$.

The specific surface areas (SSA), pore-volume, and pore size of the materials were measured by N₂ adsorption-desorption isotherms using a Micromeritics ASAP2020 system (Carried out in the Italian lab, which is different from the Belsorp Mini II apparatus in 3.3.3). Before analysis, the samples were degassed in a vacuum at 250 °C for 2 h, then the measurement was performed at liquid nitrogen temperature (-196 °C). The Brunauer–Emmett–Teller (BET) method was used to calculate the SSA. The BJH method was applied to estimate the pore volume and average pore size.

The crystalline structure of calcined, reduced, and spent samples was determined by Powder X-ray diffraction patterns (XRD), performed on a Bruker D5000 diffractometer equipped with a Cu K α anode and graphite monochromator (different from the apparatus in 3.3.5). The data were recorded in a 2θ range of 10°-80° or 20°-80° (depending on the crystalline nature of the samples) with a step size of 0.05° and time per step of 5 s. The crystalline phases of samples were analyzed according to ICSD files (Inorganic Crystal Structure Database). The mean crystallite size was calculated by the Debye-Scherrer equation shown in Eq. 13 (3.3.5).

The reducibility of the catalysts was evaluated by temperature-programmed reduction (H₂-TPR) measurements. The experiments were carried out in a Micromeritics Autochem 2950HP apparatus (different from the apparatus in 3.3.1) equipped with a thermal conductivity detector (TCD).

Before the TPR procedure, the samples (125 mg) were pretreated with the gas mixture 5% O₂/He (50 mL/min) at 350 °C for 30 minutes, then the furnace was cooled down to room temperature under pure He flows. After pretreatment, the samples were heated from ambient temperature to 1050 °C with a heating rate of 10 °C/min under the gas mixture of 5% H₂/Ar (30 mL/min). The H₂ consumption values were calculated, with a precision of $\pm 10\%$, by integration of the TPR curves registered by TCD through a calibration procedure. On the basis of H₂ consumption in the α peak, the oxygen vacancy content (%), V_0 (%) was calculated according to the Eq. (5.1.1):

$$V_0(\%) = \frac{(\text{mmol O}_2 - /g_{\text{cat}})}{(\text{total mmol O}_2 - /g_{\text{cat}})} * 100 \quad \text{Eq. (5.1.1)}$$

where the mmol O²⁻/g_{cat} correspond to the mmol of H₂/g_{cat} from α peak and the total mmol O²⁻/g_{cat} where calculated on the basis of CeO₂ or CeO₂-Y content/g_{cat}).

Furthermore, the basicity of catalysts was investigated through CO₂ temperature-programmed desorption (CO₂-TPD) carried out in a BEL-M instrument as shown in 3.3.2 of Chapter 3 (BEL Japan Inc.) equipped with a thermal conductivity detector (TCD). Prior to adsorption, the samples (60 mg) were reduced under 5% H₂/Ar flow (50 mL/min) at 550 °C. Then, the furnace was cooled down to 80 °C under the same condition, following pretreatment under pure He (50 mL/min) for 15 min. Afterward, the adsorption of CO₂ was performed in a CO₂ mixture (10 % CO₂/He, 50 mL/min) for 1 h, then, pure He was then used to remove the physically adsorbed CO₂ for 30 min at 80 °C. Finally, the temperature-programmed desorption procedure was carried out from 80 °C to 550 °C with a heating rate of 10 °C/min under pure He flow of 50 mL/min.

Also, transmission electron microscopy (TEM) and Energy Dispersive X-ray spectroscopy (EDX) analyses were carried out with JEM-2010 and JEM-2100Plus (JEOL, Tokyo, Japan) transmission

electron microscopes shown in 3.3.7 of Chapter 3 for the reduced catalysts. Before measurement, the samples were reduced (reduction condition: 550 °C for 1 h in 5% H₂/Ar).

The X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Microtech ESCA 3000Multilab spectrometer, equipped with a dual Mg/Al anode, with an excitation source of unmonochromatized Al K α radiation (1486.6 eV). See 3.3.8 of Chapter 3 for more detail.

Moreover, thermogravimetric analyses (TGA) of the CeO₂ supported catalysts, previously reduced at 550 °C for 1 h, were performed in a TGA/DSC1 STAR System (different form 3.3.9 in Chapter 3) from Mettler Toledo Inc. The sample of 15 mg was pre-treated in N₂ (30 mL/min) from 25 °C to 500 °C with a heating rate of 10 °C/min, holding time at 500 °C for 15 min, then, it was cooled down under N₂ atmosphere to 150 °C. At 150 °C, the sample was saturated with pure O₂ (30 mL/min) for 1 h and cooled to 25 °C still under O₂. Finally, the sample was heated, under N₂ (30 mL/min), from room temperature up to 600 °C (ramp rate 5°C/min), thus, the removal of physical and chemisorbed oxygen species occurred and the weight loss was taken into account in order to evaluate the surface oxygen vacancies content of the sample. The evolution of gaseous species occurring during the above four steps was monitored by online mass quadrupole (Thermostar TM, Balzers).

5.3 Elemental content, textural properties, structural parameters, and surface compositions of the catalysts

As determined by XRF analyses, the real loading of Ni and Y in the prepared catalysts was equal to the nominal one $\pm 10\%$. In Table 5.2, the XRF-derived chemical composition is listed. The textural properties of the supports and calcined catalysts were measured by the N₂

adsorption/desorption technique. The SSA, pore volume, and average pore size of the supports and catalysts are displayed in Table 5.1. The results show that the SSA, pore volume, and pore diameter values of Y-modified supports increase with the increase of yttrium loading from 0.5 to 5.0 wt % of Y. The textural properties of the calcined catalysts and supports were measured by the N₂ adsorption/desorption technique. The specific surface areas (SSA), pore volume, and average pore size of such samples are displayed in Table 5.1. It results that the SSA, pore volume, and pore diameter values of Y-modified catalysts increase with the increase of yttrium loading from 0.5 to 2.0 wt.% of Y, then surface area and pore volume slightly decrease for 5 wt.% of Y compared to those of yttrium-free sample, while still higher pore diameter was observed for such sample, suggesting a change in the pore shape occurring at such high Y content. The highest values were obtained for the 5Ni/CeO₂-Y2.0% sample that is characterized by SSA of 78.9 m²/g, pore volume equal to 0.29 cm³/g, and pore diameter of 12.9 nm. This finding suggests that yttrium promotes the improvement of textural properties of Ni/CeO₂ based catalysts. Meanwhile, 5Ni/Y₂O₃ shows the lowest surface area and porosity.

Positive effects induced by yttrium on the textural properties of different types of supports were also reported in the literature [44,50,250]. Swirk et al. [250] studied the effect of Y on Ni-based double-layered hydroxides for dry reforming of methane and found that doping Y inside the matrix promotes the increase of BET surface area. Similar results were found for Ce and Y promoted double-layered hydroxides showing higher BET surface area as compared to the Ce-promoted material without the presence of Y [51].

Table 5.1 Textural properties of the calcined catalysts.

Catalyst	SSA (m ² /g) ^a	Pore Volume (cm ³ /g) ^b	Pore diameter (nm) ^c
CeO ₂	56.1	0.17	11.2
CeO ₂ -Y0.5%	65.3	0.22	11.9
CeO ₂ -Y1.0%	67.5	0.22	12.0
CeO ₂ -Y2.0%	90.5	0.34	13.1
CeO ₂ -Y5.0%	90.4	0.33	13.0
Y ₂ O ₃	74.7	0.18	4.7
5Ni/CeO ₂	45.7	0.14	10.3
5Ni/CeO ₂ -Y0.5%	52.7	0.18	11.5
5Ni/CeO ₂ -Y1.0%	55.9	0.19	11.6
5Ni/CeO ₂ -Y2.0%	78.9	0.29	12.9
5Ni/CeO ₂ -Y5.0%	69.7	0.27	12.4
5Ni/Y ₂ O ₃	32.8	0.12	10.6

^a The specific surface area (SSA) was calculated by the BET method.

^b The pore volume and ^c pore diameter were calculated by the BJH method applied to the desorption curves.

In order to investigate the structural properties of the catalysts, XRD measurements were registered for calcined, reduced, and spent samples. The XRD patterns are presented in Fig. 5.1.1-5.1.2 (calcined), Fig. 5.2 (reduced) and Fig. 5.3 (spent, after methanation tests), respectively, along with the ICSD reference patterns of NiO (no. 24018), metallic Ni (no. 41508), CeO₂ (no. 28753), Y₂O₃ (no. 193377) and Ce_{0.9}Y_{0.1}O_{1.95} (no. 28808) solid solution. Depending on the nature of catalysts and on the treatment, different angular ranges are displayed.

From Fig. 5.1.1a,b, distinct diffraction peaks of CeO₂ were found for all the catalysts, while signals of the Y₂O₃ crystalline phase were detected only for the Ni/Y₂O₃ sample. In Fig. 5.1.1b the

diffraction pattern of Ni/CeO₂-Y 5.0% was plotted for comparison to exclude any segregation of the yttria phase. No features at $2\theta=43.25^\circ$ corresponding to nickel oxide (NiO) were detected, suggesting high dispersion of nickel species. As for Y-modified CeO₂ supported Ni-based catalysts, as it can be seen in Fig. 5.1.2a, where the enlarged patterns in the angular range $27-30^\circ 2\theta$ are reported, the Y doping does not induce any important changes in the CeO₂ structure. The main peaks (111) are all centered between $28.55^\circ 2\theta$ (CeO₂ ICSD reference no. 28753, cubic, space group FM-3M) and $28.57^\circ 2\theta$ (Ce_{0.9}Y_{0.1}O_{1.95} ICSD reference no. 28808, cubic, space group FM-3M)) so it cannot be excluded that at the highest Y loading (5wt%) possibly a ceria-yttria solid solution is formed. Indeed, thanks to the similar ionic radius some Ce⁴⁺ ions can be replaced by Y³⁺ with oxygen vacancies formation to compensate for the excess negative charge [51,327]. However, due to the relatively low crystallinity of the samples, no structural refinements were performed. Furthermore, according to ICSD files (references no. 28753 and no. 28808) the structural parameters, d_{111} values, for CeO₂ and Ce_{0.9}Y_{0.1}O_{1.95} references are almost coincident, 3.122 and 3.1207 Å, respectively, so no significant differences are expected in our experimental patterns. On the other hand, if the introduction of Ni²⁺ into the ceria lattice should occur, a decrease of the lattice parameter of ceria is expected due to its smaller ionic radius (0.69 Å), however, it would generate new oxygen vacancies inducing a small expansion of the cell, so the two effects would cancel out.

Meanwhile, a broadening of the diffraction peaks of CeO₂ was also identified with the increasing dopant of yttrium, as can be seen from Fig. 5.1.2a. Accordingly, the particle sizes of CeO₂ in calcined catalysts decreased as the increased content of Y, and the smallest size was obtained for 5Ni/CeO₂-Y5% sample (see Table 5.2). This could partially interpret the increasing BET surface area and porosity values reported in Table 5.1. As for Y₂O₃ supported Ni catalyst, it can be affirmed

that no distinct diffraction peaks of NiO at 43.25° neither at 37.25° 2θ are detectable even magnifying the patterns (see Fig.5.1.2b where the NiO reference file is compared with patterns for 5Ni/Y₂O₃ and Y₂O₃ characterized by a peak at 43.39° 2θ).

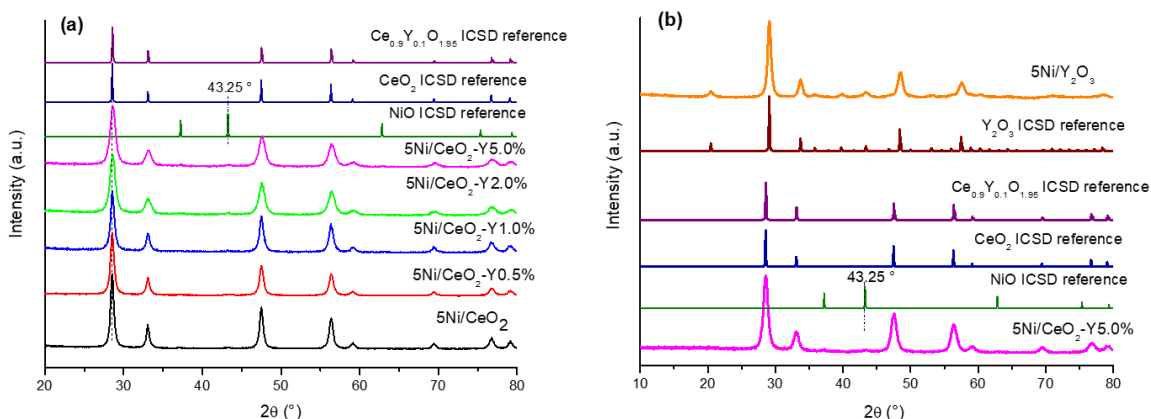


Figure. 5.1.1 XRD patterns of the catalysts calcined at 550 °C for 5 h : (a) Ni/CeO₂ and NiCeO₂-Y(0.5-5%) catalysts; (b) Ni/Y₂O₃ and Ni/CeO₂-Y5%. The reference ICSD files are also displayed.

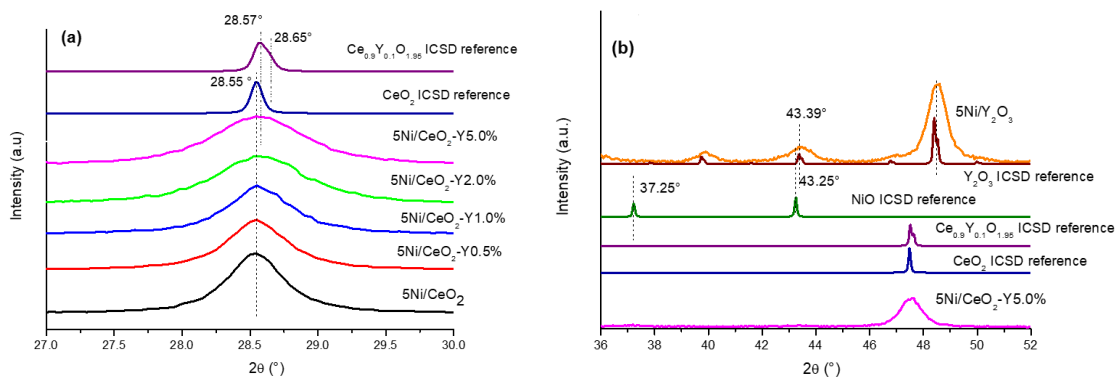


Figure. 5.1.2. XRD patterns in the enlarged range (a) 27-30 °, (b) 36-52 ° 2θ of the catalysts calcined at 550 °C for 5 h

The XRD patterns of the reduced catalysts are presented in Fig. 5.2a,b where the enlarged ranges from 42 to 52 and 20 to 52° 2θ are displayed for Ni/CeO₂, Ni/CeO₂-Y (0.5-5%), and Ni/Y₂O₃,

respectively, along with the ICSD reference files. Such angular ranges were chosen in order to detect any features ascribable to metallic Ni. No diffraction peaks of metallic nickel at $44.4^\circ 2\theta$ are detectable in any case which means that the active nickel metals keep highly dispersed on the supports after reduction.

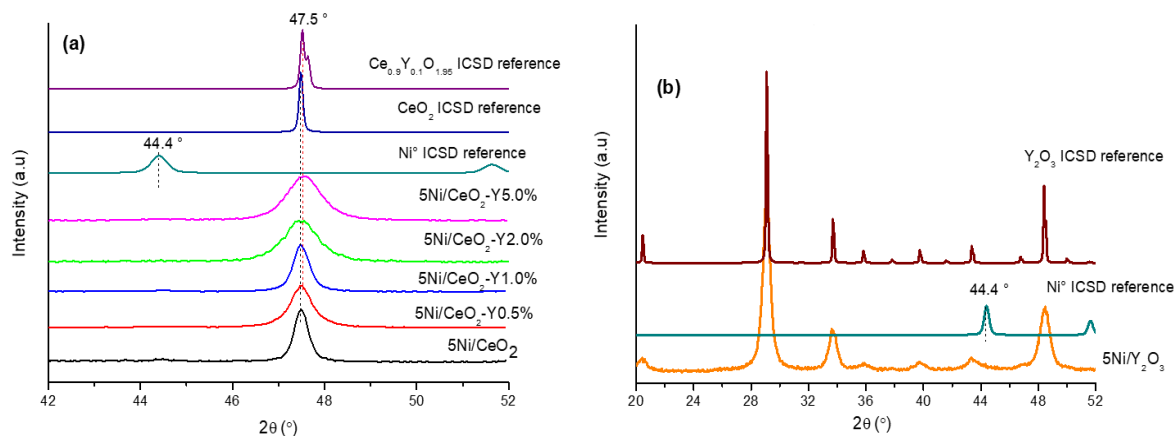


Figure. 5.2. XRD patterns of the catalysts reduced at 550 °C for 1 h in the gas mixture 5% H₂/Ar (100 mL/min).

a) Ce based catalysts, b) 5Ni/Y₂O₃

For spent catalysts (after methanation reaction) similar behavior as for the reduced catalysts was confirmed, see XRD patterns shown in Fig. 5.3.

No diffraction peaks of NiO at 43.25° and $37.25^\circ 2\theta$ nor of Ni⁰ at $44.4^\circ 2\theta$ were detected for Y-modified catalysts, meaning that no sintering of Ni specie (as Ni or as reoxidized NiO) occurs during the catalytic test. This finding confirms the high dispersion of nickel species and the occurrence of metal-support interaction stabilizing Ni even after reduction treatment and catalytic test.

The particle sizes of CeO₂, CeO₂-Y, and Y₂O₃ were calculated for calcined, reduced, and spent catalysts by the Debye-Scherrer equation and are listed in Table 5.2. The particle size for calcined samples decreases gradually with the increase of Y content, with the smallest size obtained on a 5 wt.% Y-modified sample. For the reduced and spent samples, similar trends were also registered by comparing Ni/CeO₂-Y samples at different Y loading, but the smallest particle size of the support was found on Ni/CeO₂-Y 2.0%.

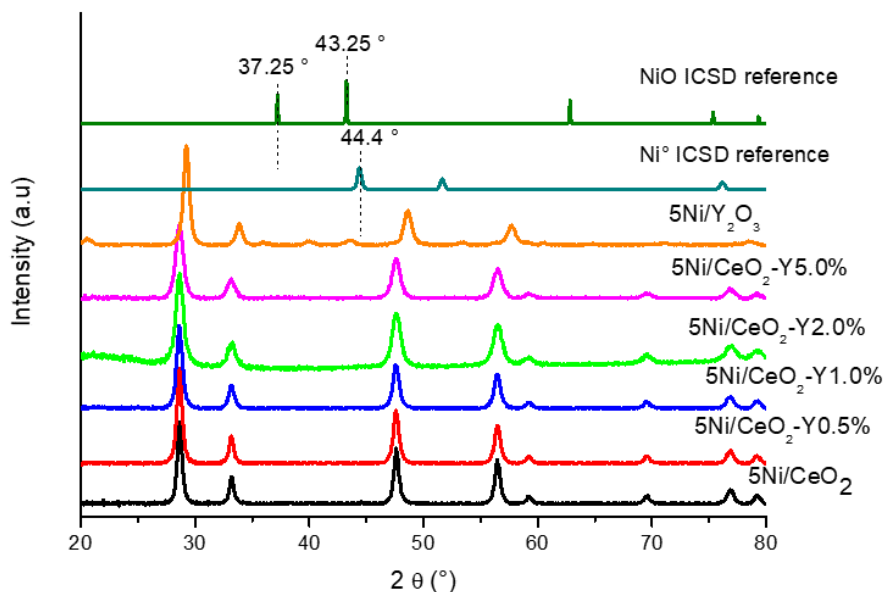


Figure. 5.3. XRD patterns of catalysts after activity test; Reactivity condition: CO₂/H₂//Ar=15/60/25(vol./vol.), flow rate=100 mL/min, WHSV=60,000 mL·g_{cat}⁻¹·h⁻¹, atmospheric pressure, temperature range from 200 to 450 °C.

By comparing the particle size of the support for each catalyst as calcined, reduced, or spent, it results that for Ni/CeO₂ the size slightly increased upon reduction or catalytic test, while for Ni/CeO₂-Y and Ni/Y₂O₃ catalysts, the particle sizes were nearly the same.

Table 5.2 Ni and Y loadings of the calcined catalysts as determined by XRF analysis and support particle size of the calcined, reduced, and spent samples

Catalyst	Ni (wt.%) ^a	Y (wt.%) ^a	Particle size of the support (nm) ^b		
			Calcined	Reduced	Spent
5Ni/CeO ₂	4.95±0.5	-	17.2	18.0	18.1
5Ni/CeO ₂ -Y0.5%	4.95±0.5	0.5±0.05	16.1	16.0	16.3
5Ni/CeO ₂ -Y1.0%	4.95±0.5	1.0 ±0.1	16.0	16.2	14.8
5Ni/CeO ₂ -Y2.0%	4.95±0.5	2.0±0.2	11.9	11.6	11.7
5Ni/CeO ₂ -Y5.0%	4.95±0.5	5.0±0.5	11.4	11.6	12.1
5Ni/Y ₂ O ₃	4.95±0.5	nd	13.3	13.7	13.6

^a Obtained from XRF analysis^b Calculated by Debye-Scherrer equation fitting the 4 strongest peaks of CeO₂ or Y₂O₃ in XRD patterns

In brief, the XRD results of calcined, reduced, and spent samples indicate that the nickel species keep highly dispersed before/after reaction for all catalysts and the particle sizes of supports decreased due to Y doping. The unaffected structural properties of the catalysts after test illustrate the metal-support interaction in the catalysts, which suppress the sintering of catalyst particles [194].

The X-ray photoelectron spectroscopy (XPS) analysis performed over calcined samples was expected to identify the surface compositions and oxidation states of the catalysts. The region of Ce3d, Ni2p, Y3d, and O1s of the catalysts were recorded and analyzed by peak fitting procedure. The percentage of Ce (III)/Ce (IV), lattice oxygen (OL)/surface chemisorbed hydroxyl species (OOH), Ni/Ce or Y/Ce, the binding energy of O1s, Ni2p_{3/2}, and Y3d_{5/2} are listed in Table 5.3. The

survey spectrum and the Y3d, O1s, Ni2p, and Ce3d regions of 5Ni/CeO₂-Y2.0% are shown in Fig. 5.4.

As shown in Fig. 5.4, the doublet of Y3d with two peaks located at 157.4 eV (Y3d_{5/2}) and 159.3 eV (Y3d_{3/2}) represents the Y³⁺ species [354]. There is no significant difference regarding the Y3d_{5/2} position (presented in Table 5.3) between Y-modified catalysts and pure Y₂O₃ supported catalysts except slight shifts (± 0.2 eV), which comply with other reports [355]. The presence of cerium does not influence the position of Y3d peaks, indicating a weak interaction between the two elements. The Y/Ce atomic ratio increase is not linear with the increase of Y content. Uneven distribution of Y between bulk and surface or the presence, in the higher Y content samples, of bigger particles of Y₂O₃ may be responsible for this behavior.

The Ce3d region of 5Ni/CeO₂-Y2.0% shows the typical complex profile, consisted of 10 peaks, which is arisen by the ligand-to-metal charge transfer transitions [356]. Many different approaches deal with the fitting of the Ce3d peak [357,358], in this study, the approach reported by Burroghs et al. [358] was used, with ten components that take into account the spin-orbit splitting of Ce3d_{5/2}, Ce3d_{3/2}, and others splitting caused by a redistribution of the entire energy spectrum after a core hole is created. There are four components (labeled as v⁰, u⁰, vⁱ, uⁱ) attributed to Ce (III) and six components (labeled as v, u, vⁱⁱ, uⁱⁱ, vⁱⁱⁱ, uⁱⁱⁱ) attributed to Ce (IV). The data were fitted using the constrains between the corresponding components 3d_{5/2}-3d_{3/2} given by Preisler et al. [359] The Ce (III) percentages calculated as $(Iv^0 + Iv^i) / (Iv^0 + Iv^i + Iv + Iv^{ii} + Iv^{iii}) * 100$, showed in Table 5.3, ranges between 9 and 19 %, and it can be concluded that the Ce (III) concentration increases with the increasing yttrium content, which was also demonstrated in other literature [360]. The dopant of Y promotes the formation of Ce³⁺, thus, more oxygen vacancies are created [361].

The O1s region contained two contributions, one due to lattice oxygen (OL) with BE (Binding Energy) of 529.4 ± 0.3 eV [355,362], the other attributed to the hydroxyl species chemisorbed on the surface (OOH) with BE of 531.5 ± 0.4 eV [362]. As shown in Table 5.3, the relative amount of OOH increases with increasing Y up to 1-2% (within the experimental error) which could be assigned to the increase of Ce³⁺. Because the oxygen species adsorbed on Ce³⁺ showed higher stability than that of Ce⁴⁺ [363].

The Ni2p_{3/2} profile with a peak centered at 855.0 ± 0.2 eV along with a shake-up peak at 862 ± 0.5 eV is typical of Ni(II) [364]. Compared to the 5Ni/CeO₂, the binding energy of Ni2p_{3/2} for the Y-modified catalyst shows a small decrease (0.2-0.5 eV) in Table 5.3, indicating a slightly increased interaction between the Ni and the support [350,365].

Such finding further confirms the occurrence of metal-support interaction in Ni/CeO₂-Y promoted catalysts as argued based on XRD data.

The Ni/Ce atomic ratio decreases with the rise of Y content of the surface of the catalysts, except for Ni/CeO₂-Y1.0%. This fact could be attributed to different factors, such as slightly bigger Ni particles, a different distribution of Ni on the surface due to changes in morphology, or the migration of Ni into the bulk likely forming Ni-Ce-O solid solution.

Table 5.3. XPS derived Ce (III) and Ce (IV) percentage, the binding energy of O1s, Ni2p_{3/2}, and Y3d_{5/2} in eV and Ni/Ce and Y/Ce atomic ratio of the various Ni catalysts in the calcined state. In parenthesis, the relative percentage between OL and OOH is indicated.

Catalyst	Ce(III)-Ce(IV)	O1s (eV)		Ni2p _{3/2} (eV)	Ni/Ce	Y3d _{5/2} (eV)	Y/Ce
		OL	OOH				
5Ni/CeO ₂	11%-89%	529.5 (54%)	531,9 (46%)	855.3	0.23	-	-
5Ni/CeO ₂ - Y0.5%	9%- 91%	529.6 (54%)	531,4 (45%)	854.9	0.16	157.3	0.54
5Ni/CeO ₂ - Y1.0%	12%-88%	529.6 (40%)	531.3 (60%)	854.8	0.23	157.6	0.72
5Ni/CeO ₂ - Y2.0%	16% - 84%	529.1 (45%)	532.7 (54%)	855.1	0.17	157.4	0.68
5Ni/CeO ₂ - Y5.0%	19 %-81%	529.7 (60%)	531.5 (40%)	855.0	0.16	157.7	0.86
5Ni/Y ₂ O ₃	-	529.4 (45%)	531.9 (54%)	855.2	-	157.4	-

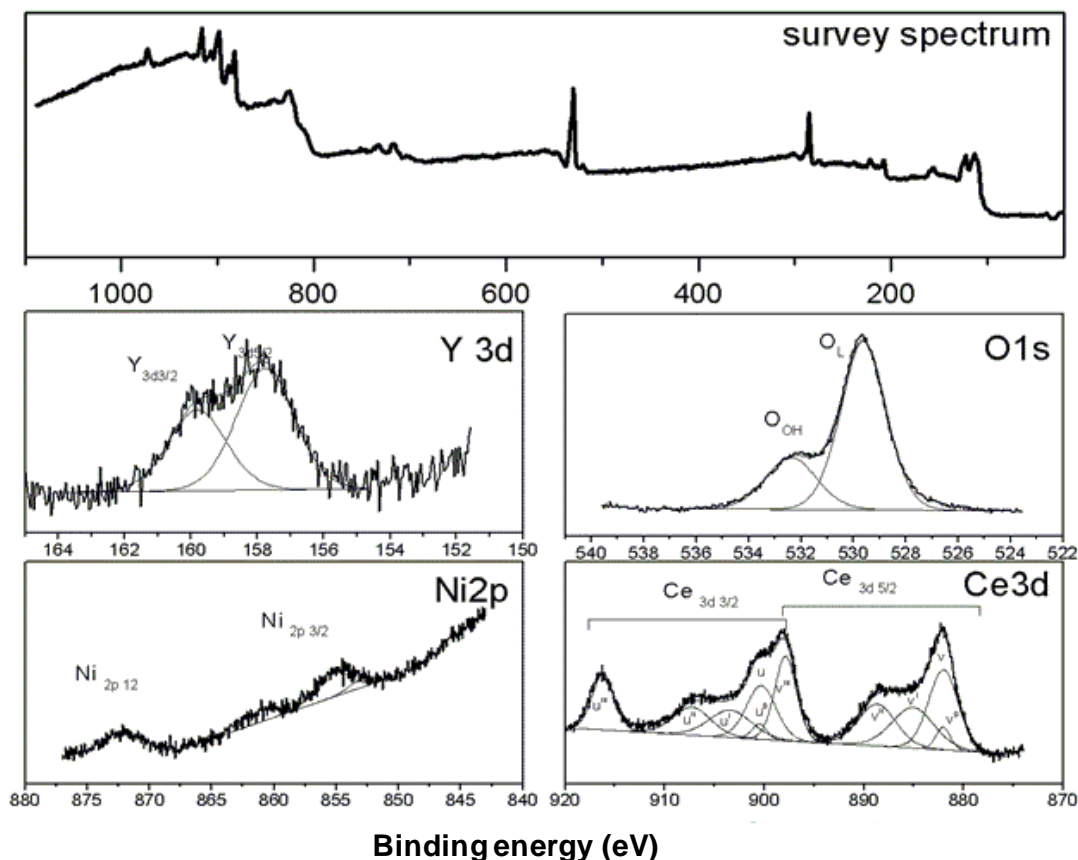


Figure. 5.4. XPS survey spectrum and XPS Y3d, O1s, Ni2p, and Ce3d profiles of the calcined 5Ni/CeO₂-Y_{2.0}% catalyst.

5.4 On the reducibility of calcined catalysts

To study the reducibility of the calcined catalysts and determine the optimal reduction condition for CO₂ methanation, temperature-programmed reduction in H₂ (H₂-TPR) was performed on the calcined samples. The H₂-TPR profiles are displayed in Fig. 5.5, the temperatures at the maxima of reduction peaks and H₂ consumption values are listed in Table 5.4. To get more insight into the effect of Ni on the reduction properties of the supports, TPR experiments were registered also over selected supports as shown in Fig.5.5b and Table 5.4. As shown in Fig. 5.5, there are 3 main peaks

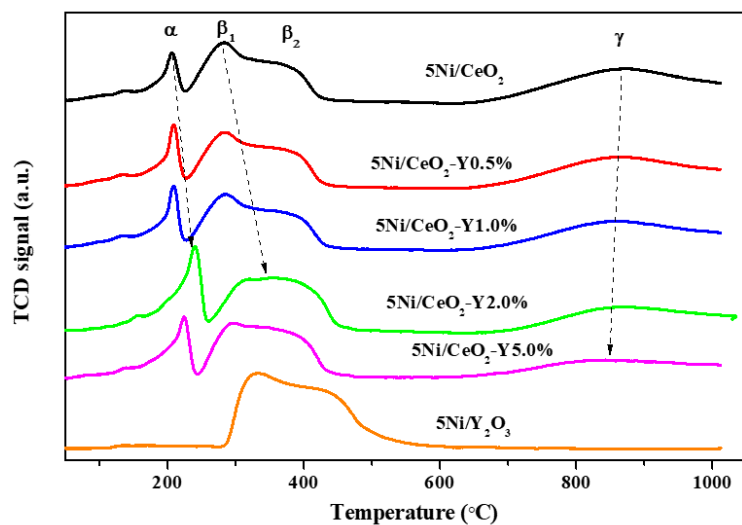
over Ni/CeO₂ and Ni/CeO₂-Y catalysts, which are labeled as α , β , and γ in the figure. The α peak, which started at a very low temperature (ca. 39 °C) over 5Ni/CeO₂ sample, was ascribed to the reduction of oxygen species chemisorbed on the oxygen vacancies that likely are generated by the partial substitution of CeO₂ lattice by Ni²⁺ and Y³⁺ species, resulting in Ni-Ce-O solid solution or Y-Ce-O solid solution [201,350,366,367].

It is worth noting that the α peak shifts toward higher temperature with the increase of Y loading until 2 wt.% of Y, and then shift a little toward lower temperature for the sample with 5 wt.% of Y. Moreover, the H₂ consumption of the α peak (see Table 5.4) gradually increased with Y loading until 2 wt.% of Y, with the highest value. This finding could be explained by an increased concentration on the surface of the catalysts of Ce³⁺ ions able to chemisorb oxygen species reducible below 250 °C (see TGA curves and XPS analysis) and agrees with the change of the morphology of Ni/CeO₂-Y catalysts by increasing the Y loading from 0 up to 5wt % (see TEM characterization). On the other hand, the shift of the α peak toward higher temperature until 2 wt.% of Y and the highest hydrogen consumption registered for such a peak suggest that doping ceria with 2 wt % of Y produces the highest oxygen vacancy concentration with strongly chemisorbed oxygen.

It is also worth noting that no α peaks at around 200-250 °C were observed in the TPR profiles of CeO₂ and CeO₂-Y doped oxides (see Fig 5.5b), supporting the active role of Ni²⁺ in promoting the creation of oxygen vacancies in the catalysts.

On the basis of H₂ consumption in the α peak, considering that 1 mmol of H₂ is supposed to react with 1 mmol of O²⁻ species per oxygen vacancy, the V₀ content (%) was calculated based on the Eq. 5.1.1 (see 5.2) and is given in Table 5.4. A similar trend as the hydrogen consumption in the α peak was found as a function of the Y loading.

(a)



(b)

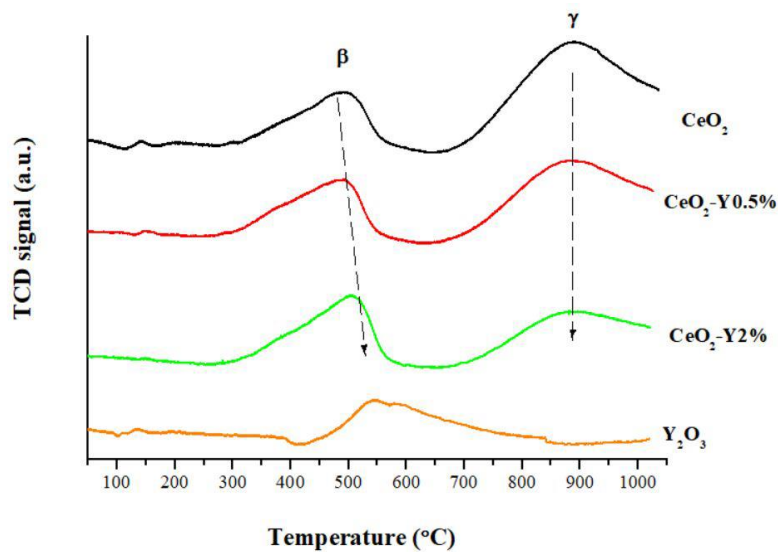


Figure. 5.5. H₂-TPR profiles of (a) catalysts and (b) selected supports; Operating condition: 5% H₂/Ar flow rate of 30 mL/min, a ramp of 10 °C/min.

The broad reduction peak, β , can be divided into 2 different features i.e. β_1 and β_2 (e.g. ca. 283 °C and 360 °C for 5Ni/CeO₂ sample) that can be assigned to the reduction of NiO species that have different intensity of metal-support interaction [350,368]. The β_1 peak can be attributed to the reduction of bulk NiO that has a weak interaction with the support or to un-interacted NiO crystallites [350,369]. The β_2 corresponds to the NiO nanoparticles in intimate contact with the support [170]. The β_1 and β_2 peaks shift towards higher temperature at higher Y loading, from 0.5 to 2 wt.%, confirming strong metal-support interaction with the best synergy achieved at 2 wt.% Y. Moreover, at high Y loading, the two features β_1 and β_2 become less defined overlapping into a single broad peak, suggesting that such a peak contains the contribution from several species that are reduced simultaneously. According to the literature and the results from Fig. 5.5b and Table 5.4 [170,350,370], the reduction of the ceria surface occurs with a maximum at ~490–505 °C. Therefore, the β peak may correspond to the concomitant reduction of nickel species and the ceria surface, and the broader the peak, such as that detected for 5Ni/CeO₂–Y2.0%, the higher the intimate contact.

At a high-temperature peak (at $T > 800$ °C), labeled γ in Fig. 5.5, is due to the bulk reduction of the CeO₂-based oxides, although reduction of some NiO species strongly interacting with the support cannot be excluded [350,371].

According to the H₂ consumption values reported in Table 5.4 and considering that the theoretical amount required for the overall reduction of NiO to metallic Ni is 0.85 mmol/g_{cat}, based on a real Ni loading equal to 5 wt%, the β reduction peak (ranging between 0.73-0.78 mmol/g_{cat}) may contain the contribution from some NiO in contact with ceria surface along with surface ceria reduction. The reduction of the remaining part of NiO together with some ceria bulk may occur at $T > 800$ °C. Similar H₂ consumptions of the β peak were registered for Ni/CeO₂ and Ni/CeO₂-Y

catalysts confirming that the catalysts contain a comparable amount of NiO particles with similar size interacting with the ceria surface. As it concerns the γ peak, the H₂ consumption decreases with the increase of Y content (0-5 wt.%), in accord with higher oxygen vacancies in the catalysts [192,350]. Such a trend was confirmed by XPS analysis (Table 5.3). and by TPR of selected supports. From the values listed in Table 5.4, it can be seen that moving from CeO₂ to CeO₂-Y0.5% and CeO₂-Y 2.0%, the hydrogen consumption of the β peak gradually increased, especially for Y 2.0%, in accordance with higher SSA. Conversely, the hydrogen consumption of the γ peak decreased and, on the whole, the $\beta + \gamma$ uptake decreased in line with an increased oxygen vacancy concentration.

For 5Ni/Y₂O₃, only a broad peak between ~300-500 °C was registered with two maxima at 330 and 435 °C and according to the previous notation, we will continue to label such peaks as β 1 and β 2. For comparison, the TPR of the Y₂O₃ support was registered to show a peak centered at ~550 °C with H₂ consumption of 0.31 mmol/g_{cat} (see Figure 5.5b and Table 5.4). The H₂ consumption value of β peak for 5Ni/Y₂O₃ is 1.29 mmol/g_{cat}, which exceeds the theoretical value required for the total reduction of NiO to metallic Ni (0.85 mmol/g_{cat}) and 1.16 mmol/g_{cat} (corresponding to the sum 0.85 plus 0.31 mmol/g_{cat}, i.e., the H₂ consumption of the yttria oxide), suggesting that new oxygen vacancies are created in the Y₂O₃ after Ni deposition. Bellido et al. [325] studied the effect of Y₂O₃-ZrO₂ composition on Ni/Y₂O₃-ZrO₂ catalysts and they found that the reduction of pure Y₂O₃ support only accounted for a small fraction of the reduction in the H₂-TPR measurement. However, the reduction behavior of the Ni/Y₂O₃-ZrO₂ supports was significantly influenced by the interaction among the species and the introduction of Y³⁺ into ZrO₂ and likely of Ni²⁺ create new oxygen vacancies to preserve overall electroneutrality. Based on the literature [325], the relatively low temperature of the peak maximum (333 °C) registered for

5Ni/Y₂O₃ and the H₂ consumption higher than that required for NiO reduction (Table 5.4) were attributed to the presence of a high number of oxygen vacancies on the support interacting with NiO.

Table 5.4. Reduction temperatures at the peak maximum (T_{\max}) and H₂ consumption values of the calcined catalysts derived from H₂-TPR.

Catalyst	T_{\max} (°C)			H ₂ consumption (mmol/g _{cat})			V_0 (%) ^a
	α	β	γ	α	$\beta(\beta_1+\beta_2)$	γ	
5Ni/CeO ₂	207	283	873	0.26	0.76	0.73	2.36
5Ni/CeO ₂ - Y0.5%	209	286	861	0.29	0.73	0.67	2.62
5Ni/CeO ₂ - Y1.0%	209	286	861	0.30	0.73	0.62	2.70
5Ni/CeO ₂ - Y2.0%	240	354	872	0.44	0.75	0.59	3.95
5Ni/CeO ₂ - Y5.0%	225	297	843	0.33	0.78	0.43	2.92
5Ni/Y ₂ O ₃	-	333	-	-	1.29	-	-
CeO ₂	-	490	885	-	0.33	0.76	-
CeO ₂ -0.5% Y	-	492	882	-	0.36	0.68	-
CeO ₂ -2.0% Y	-	505	880	-	0.40	0.59	-
Y ₂ O ₃	-	550	-	-	0.31	-	-

^a Oxygen vacancies (%) calculated from α peak

5.5 Morphologies of the catalysts derived from TEM and HRTEM characterization

In order to gain more morphology information of the catalysts, the high-resolution transmission electron microscopy (HRTEM) and TEM analyses were conducted over the reduced samples using the same reduction condition as the activity test. The micrographs of reduced catalysts were shown in Fig.5.6-5.8.

It can be seen from Fig. 5.6 that all the catalysts contain well-defined crystallites and that the introduction of Y tailors the particle sizes of CeO₂ in the catalysts. In the absence of Y as shown in Fig. 5.6a, the CeO₂ particles were nanoparticles (NPs) as irregular polyhedra with some aggregated particles exceeding 50 nm. In Fig. 5.6b, the CeO₂ particles promoted with 0.5 wt.% of Y became smaller. Higher concentrations of Y nanorods (NRs) appeared (Fig.5.6c-e). It was difficult to evaluate the proportion of nanorods but we noted that on one side the NPs size decreased and on the other, the NRs became thinner. The influence of Y concentration on average grain size and the morphology is summarized in Table 5.5 where the measurements obtained from the TEM images are listed. The effect of the concentration of a doping element was already related by Saabari et al. [372]. The formation of nanorods with high exposed surface area detected from 1 to 2 wt.% of Y complies with the increased intensity of the α peak, attributed to the reduction of oxygen species chemisorbed on oxygen vacancies and is in line with the highest SSA of the Ni/CeO₂-Y2%. The aspects of the NRs are presented in Fig. 5.7. We see the decrease in the size of nanorods from 1 wt.% Y (Fig. 5.7a) to 5 wt.% Y (Fig. 5.7c). All catalysts are well crystallized as evidenced by the lattice planes. The nanorod of 5Ni/CeO₂-Y2% (Fig. 5.7d) reveals the (111) and (220) planes corresponding to the distance of 3.12 and 1.91 Å, respectively. The NPs as for them showed frequently the (111) facets. Therefore, Y addition does not produce significant modification into the CeO₂ lattice in agreement with XRD characterization.

For the pure Ni/Y₂O₃ sample, large aggregate nanoparticles of 10-15 nm were detected, see Fig. 5.6f.

From the reported data it can be concluded that the morphology of the reduced catalysts changed with the incorporation of Y. The particle size of CeO₂ decreased as increasing Y loading with the formation of nanorods and such trend is in accord with the increase of SSA shown in Table 5.1. As previously reported in the literature, CeO₂ morphology can be modulated depending on the preparation conditions, and nanorods formation is favored during the hydrothermal process [196].

By simple TEM analysis, the size distribution of Ni⁰ nanoparticles cannot be distinguished according to another author's report [196]. In order to obtain more detailed information on nickel particle sizes, HRTEM images and EDX spectra were recorded and are shown in Fig.5.7-5.10, where the measured sizes of Ni⁰ nanoparticles are marked, mapping was also carried out.

HRTEM images show that the Ni metallic particles are spherical and well dispersed on the support. The average size was ranging from 6-12 nm for all catalysts. The Ni metallic particles were detected by the lattice planes of 2.03 or 1.76 Å corresponding respectively to the (111) or (002) planes of the FCC (face center cubic) structure of nickel.

The EDX spectra show that the signals of Ni and Ce keep stable with the increase of Y loading, indicating again high dispersion of Ni. For the 5Ni/CeO₂-Y2.0% sample the composition homogeneity of Ni and Y was confirmed by Scanning TEM-Energy Dispersive X-ray Spectroscopy (STEM-EDX) mapping (Fig. 5.9 and Fig. 5.10).

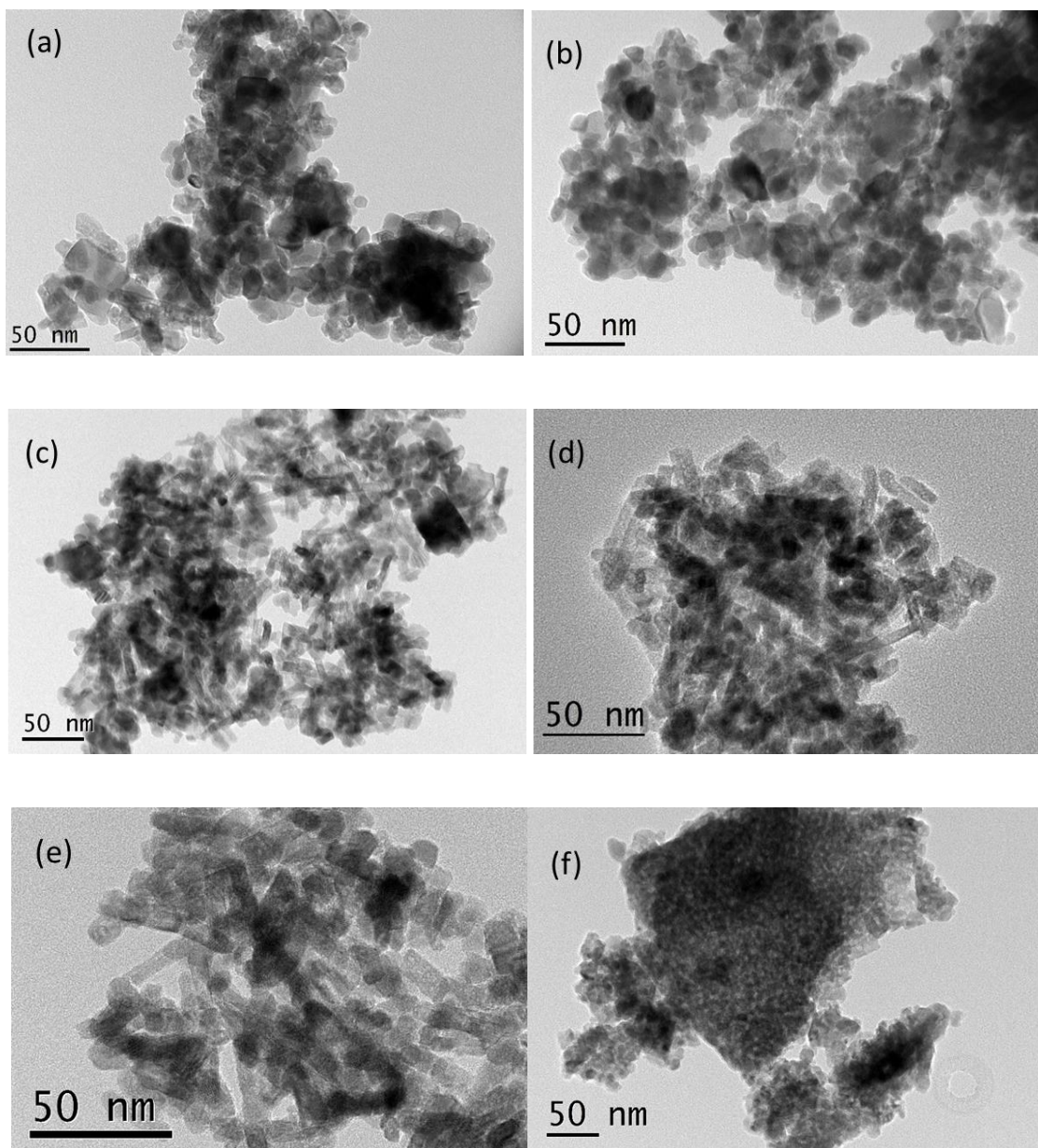


Figure. 5.6. TEM micrographs of the catalysts reduced at 550 °C for 1 h in 5% H₂/Ar (100 mL/min); (a) 5Ni/CeO₂, (b) 5Ni/CeO₂-Y0.5%, (c) 5Ni/CeO₂-Y1.0%, (d) 5Ni/CeO₂-Y2.0%, (e) 5Ni/CeO₂-Y5.0%, (f) 5Ni/Y₂O₃.

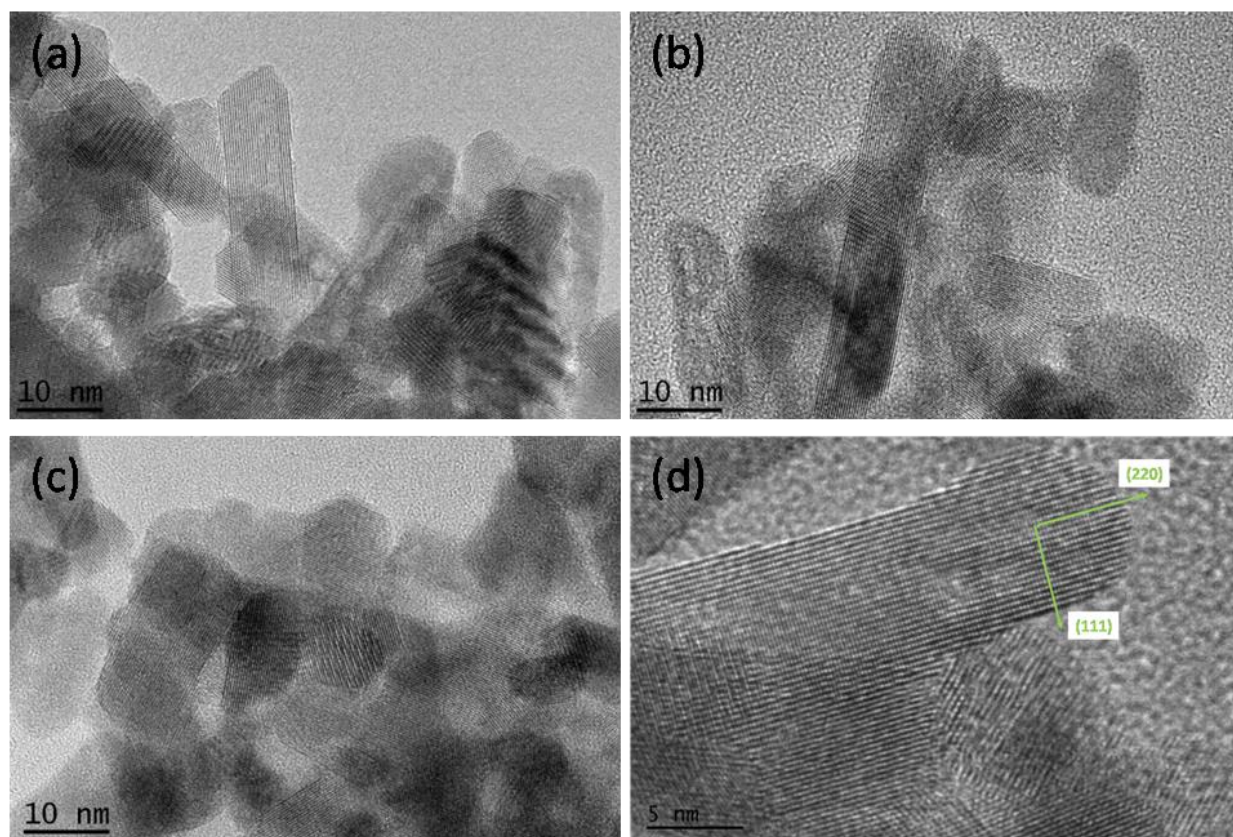


Figure. 5.7. Nano-cubes and nano-rods from HRTEM micrographs: (a) 5Ni/CeO₂-Y1.0% (b, d) 5Ni/CeO₂-Y2.0% (c) 5Ni/CeO₂-Y5.0%

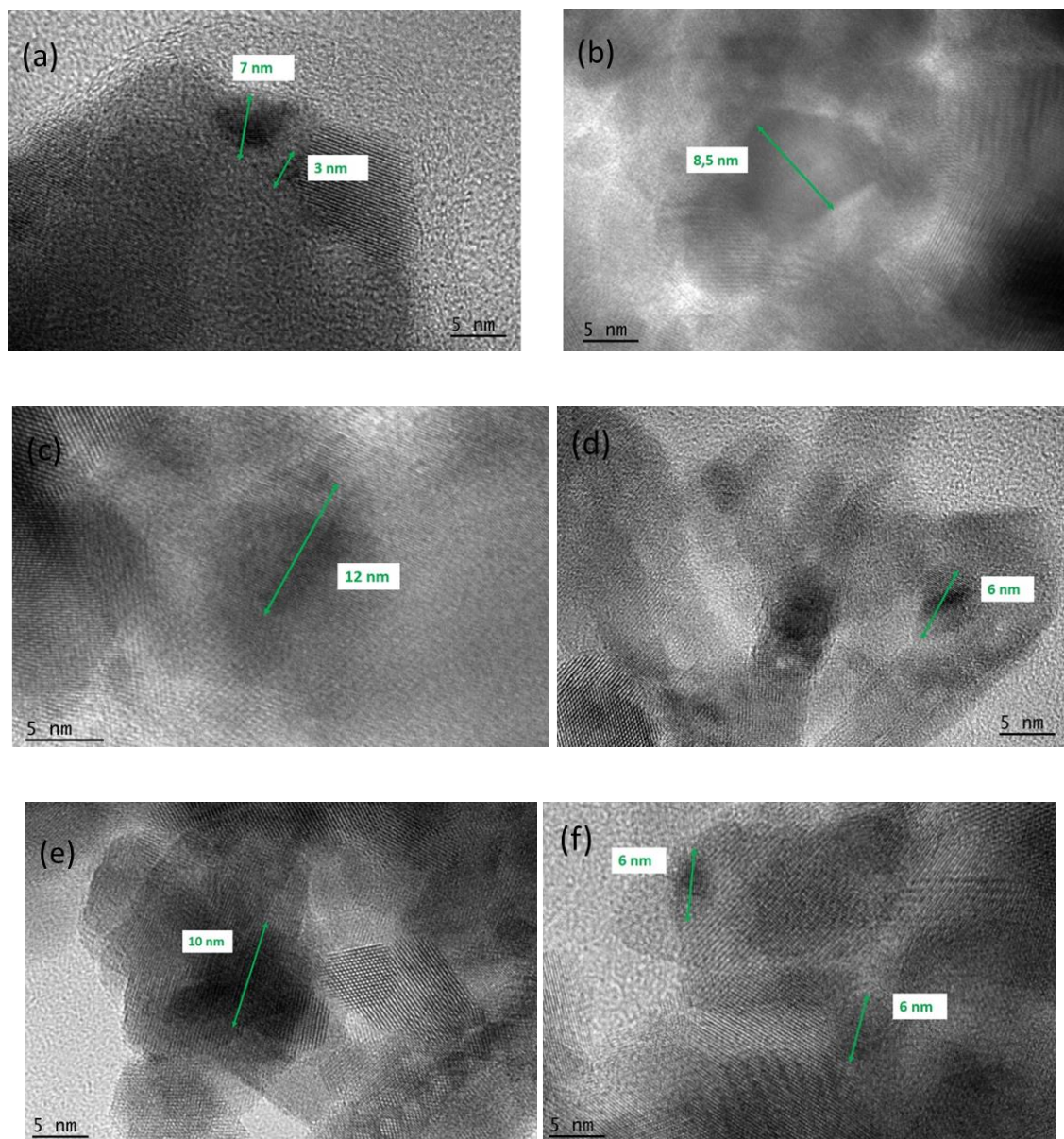


Figure. 5.8. HRTEM micrographs of the catalysts; Condition: reduced at 550 °C for 1 h in 5% H₂/Ar (100 mL/min); (a) 5Ni/CeO₂, (b) 5Ni/CeO₂-Y0.5%, (c) 5Ni/CeO₂-Y1.0%, (d) 5Ni/CeO₂-Y2.0%, (e) 5Ni/CeO₂-Y5.0%, (f) 5Ni/Y₂O₃.

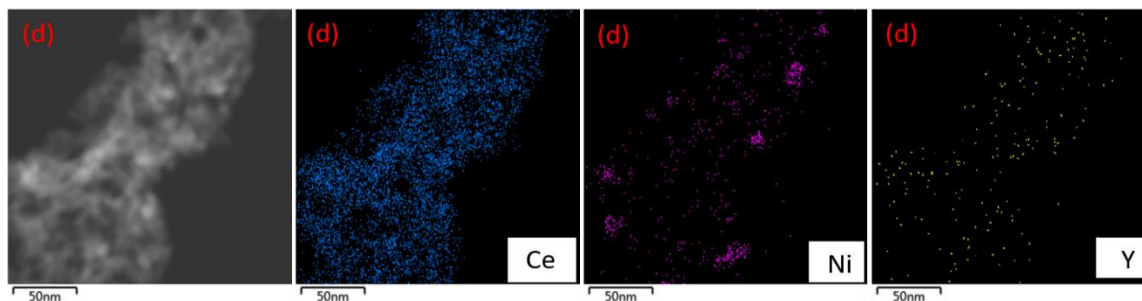


Figure. 5.9. STEM-HAADF image and STEM-EDX mapping of the catalyst, (d), 5Ni/CeO₂-Y2.0%; Condition: reduced at 550 °C for 1 h in 5% H₂/Ar (100 mL/min).

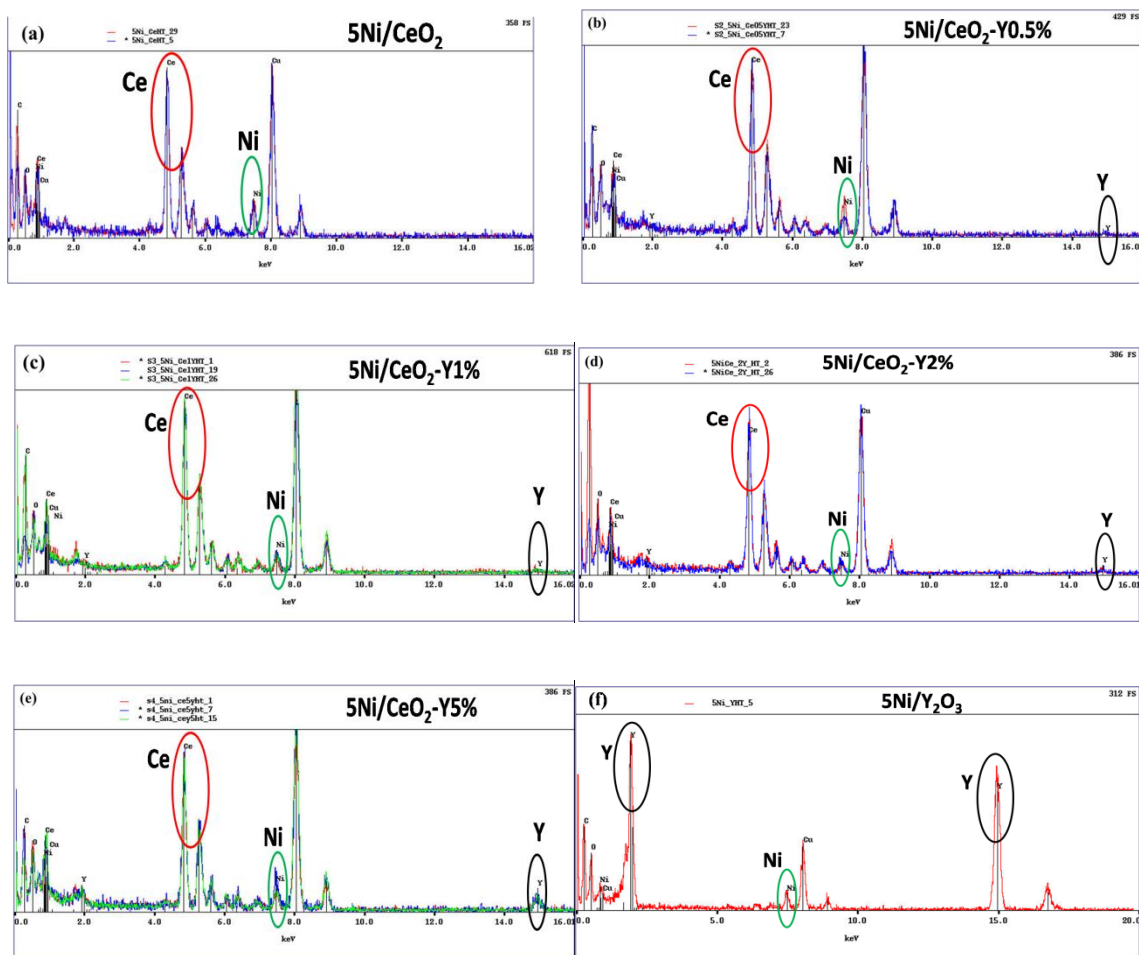


Figure. 5.10. EDX spectra of the catalysts; Condition: reduced at 550 °C for 1 h in 5% H₂/Ar (100 mL/min); (a) 5Ni/CeO₂, (b) 5Ni/CeO₂-Y0.5%, (c) 5Ni/CeO₂-Y1.0%, (d) 5Ni/CeO₂-Y2.0%, (e) 5Ni/CeO₂-Y5.0%, (f) 5Ni/Y₂O₃.

Overall, Ni⁰ resulted well dispersed on CeO₂-based catalysts as confirmed by XRD results. Moreover, Y doping promotes the decrease of the CeO₂ particle size and the formation of CeO₂ nanorods.

Table 5.5. Support particle size of the reduced samples deduced from TEM image analysis.

Catalyst	Size of Nanoparticles (nm)		Size of Nanorods (nm)	
	Min-Max	Currently	Length (min-max)	Diameter (min-max)
5Ni/CeO ₂	7 - 25	15	-	-
5Ni/CeO ₂ -Y0.5%	6 - 22	13	-	-
5Ni/CeO ₂ -Y1.0%	8 - 24	10	15 - 40	5 - 9
5Ni/CeO ₂ -Y2.0%	6 - 17	8	10 - 30	5 - 8
5Ni/CeO ₂ -Y5.0%	5 - 14	10	10 - 27	5.5 - 10
5Ni/Y ₂ O ₃	8 - 15	11	-	-

5.6 Evaluation of oxygen vacancies content and oxygen mobility by TGA analysis

In order to evaluate the surface oxygen vacancies content and the oxygen mobility of the Ni/CeO₂ supported (Y-modified and Y-free) catalysts, temperature-programmed desorption curves of adsorbed oxygen (O₂-TPD) were registered over the reduced catalysts by performing thermal gravimetric analyses (TGA). The acquired TGA profiles are displayed in Fig. 5.11.

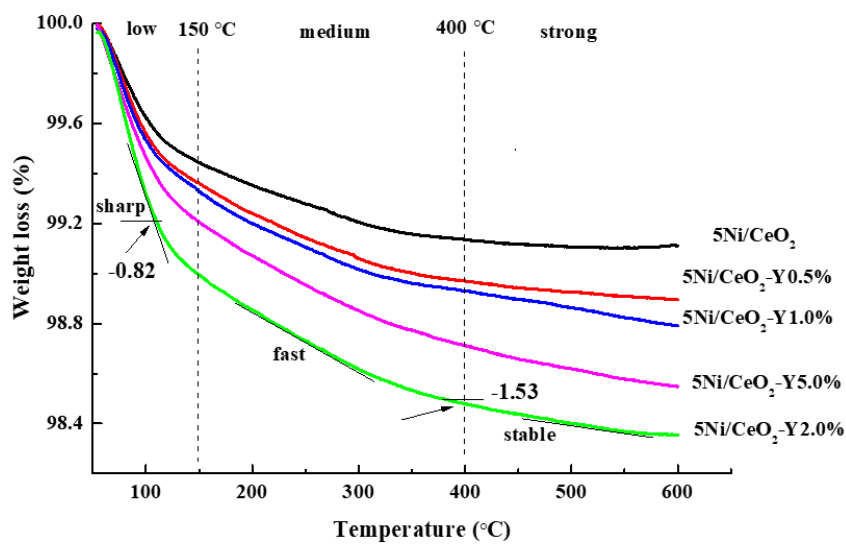


Figure. 5.11. TGA profiles under N₂ flow of reduced catalysts after saturation with pure O₂.

It can be seen from Fig. 5.11 that the reduced catalysts, after saturation with pure O₂, undergo distinct weight losses under N₂ atmosphere from room temperature until 600 °C as the desorption of adsorbed oxygen occurs. For simplicity, the curves were divided into three parts according to the weight loss slope in the different range of temperatures, i.e. sharp, fast and stable loss. So, the weight loss at the temperature below about 150 °C was ascribed to the removal of weakly adsorbed oxygen (physisorbed O₂), between ~150-400 °C desorption of chemisorbed O₂ takes place, while in the range 400-600 °C or even above 600 °C the removal of bulk oxygen species should occur [373]. In our case, a stable trend was observed up to 600 °C according to the TPR curves since ceria bulk reduction occurred above 800 °C.

At low temperature and in the range 150-400 °C, the weight loss intensity increased as a function of Y loading, from Ni/CeO₂ Y-free until 2 wt.%, then, for Y 5wt.% a decrease was observed, being the TGA curve of such sample intermediate between Y 2wt.% and Y1wt.%. Looking in detail at

the profile of 5Ni/CeO₂-Y2.0%, the sharp weight loss occurring from room temperature up to ~110 °C corresponds to -0.82% while increasing the temperature up to 400 °C, an overall weight loss of -1.53% was registered. Assuming that O₂ desorbs, the mmol of oxygen removed was calculated: below 150 °C 0.25 mmol O₂/g_{cat} (physisorbed oxygen) and in the overall 0.47 mmol O₂/g_{cat} up to 400 °C are desorbed. Therefore, the amount of chemisorbed O₂ is equal to 0.22 mmol/g_{cat}. Such value is exactly the half amount of the H₂ consumption value registered for the α peak in the TPR experiment (see Table 5.4). Considering that 1 mmol of H₂ reacts with 1 mmol of O²⁻ species per oxygen vacancy, such finding confirms that the α peak is due to the reduction of oxygen species adsorbed on the vacancies.

In conclusion, TGA analyses confirmed that Y dopant promoted the formation of oxygen vacancies in our samples, the highest content being achieved for Y 2wt.%, according to other characterizations in this study and literature results [51,373–375].

5.7 Basicity distribution of the reduced catalysts derived from CO₂-TPD analyses

To investigate the basicity of the reduced catalysts, CO₂-TPD experiments were performed on the above catalysts. The CO₂-TPD profiles are plotted in Fig. 5.12, the concentration and distribution of basic sites are listed in Table 5.6. As shown in Fig. 5.12, the CO₂ desorption curves can be divided into three regions according to the temperatures, i.e. $T < 150$ °C, between 200-450 °C and $T > 450$ °C, corresponding to the weak, medium and strong basic sites, respectively.[160,307]

It is shown that the distribution of basic sites changed significantly with the increase of yttrium loading, in particular, the CO₂ desorption peaks of Y-modified catalysts shifted towards higher temperature as the increase of Y until 2 wt.%.

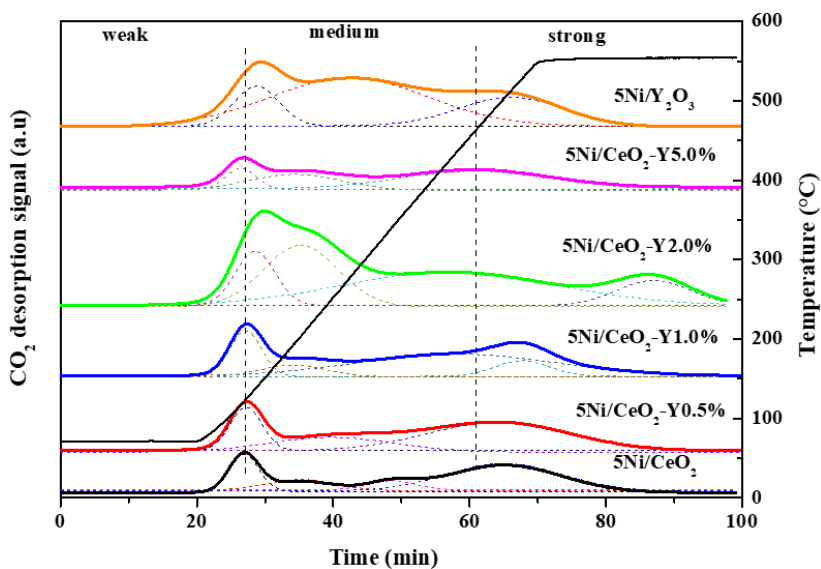


Figure. 5.12. CO₂-TPD profiles registered over reduced catalysts; Pretreatment condition: Reduction at 550 °C for 1 h in 5% H₂/Ar (50 mL/min), cooling down to 80 °C and He purging, then CO₂ adsorption under 10% CO₂/Ar for 1 h (50 mL/min).

Moreover, as reported in Table 5.6, the concentration of weak and medium + strong basic sites (as overall amount) increase as the increase of Y (up to 2.0 wt%), with slightly decreased values for Y 5.0%. The highest basicity was registered for the 5Ni/CeO₂-Y2.0% sample, while Ni/Y₂O₃ was in between Y1.0 wt% and Y 5.0 wt%.

Table 5.6. Basic sites distribution calculated from CO₂-TPD for Y-promoted catalysts after reduction at 550 °C

Catalyst	Basic sites [$\mu\text{mol/g}_{\text{cat}}$]				Distribution of basic sites [%]		
	Weak	Medium	Strong	Total basicity	Weak	Medium	Strong
5Ni/CeO ₂	18.2	13.3	63	95	19.2	14.1	66.7
5Ni/CeO ₂ - Y0.5%	22.1	8.8	87.4	118	18.7	7.5	73.8
5Ni/CeO ₂ - Y1.0%	25.1	23.7	76.7	126	20.0	18.9	61.1
5Ni/CeO ₂ - Y2.0%	35.4	75.5	140.7	251	14.1	30.0	55.9
5Ni/CeO ₂ - Y5.0%	32.3	71.3	129.0	233	13.9	30.6	55.5
5Ni/Y ₂ O ₃	30.9	55.9	77.8	165	18.8	34.0	47.2

5.8 Catalytic performance of Ni based catalysts in CO₂ methanation

The catalytic performances in CO₂ methanation reaction were investigated in a quartz reactor at atmospheric pressure introduced in Chapter 3. Prior to reaction, the sample (100 mg) was reduced in 5% H₂/Ar (100 mL/min) at 550 °C for 1 h with a heating rate of 5 °C/min. After cooling down to 200 °C, the reactant gas mixture, 100 mL/min, with a molar ratio of CO₂/H₂/Ar=15/60/25 was fed into the catalyst (WHSV=60,000 mL h⁻¹g_{cat}⁻¹). The CO₂ conversion and CH₄ selectivity were calculated according to equations in Chapter 3.

The catalytic performance in CO₂ methanation was investigated over the Ni catalysts supported over Y-modified CeO₂, pure CeO₂, and pure Y₂O₃, and the CO₂ conversion and CH₄ selectivity values are displayed in Fig. 5.13 along with the thermodynamic curves given for comparison. These results are in line with those presented in the literature in similar experimental conditions Table 5.7.

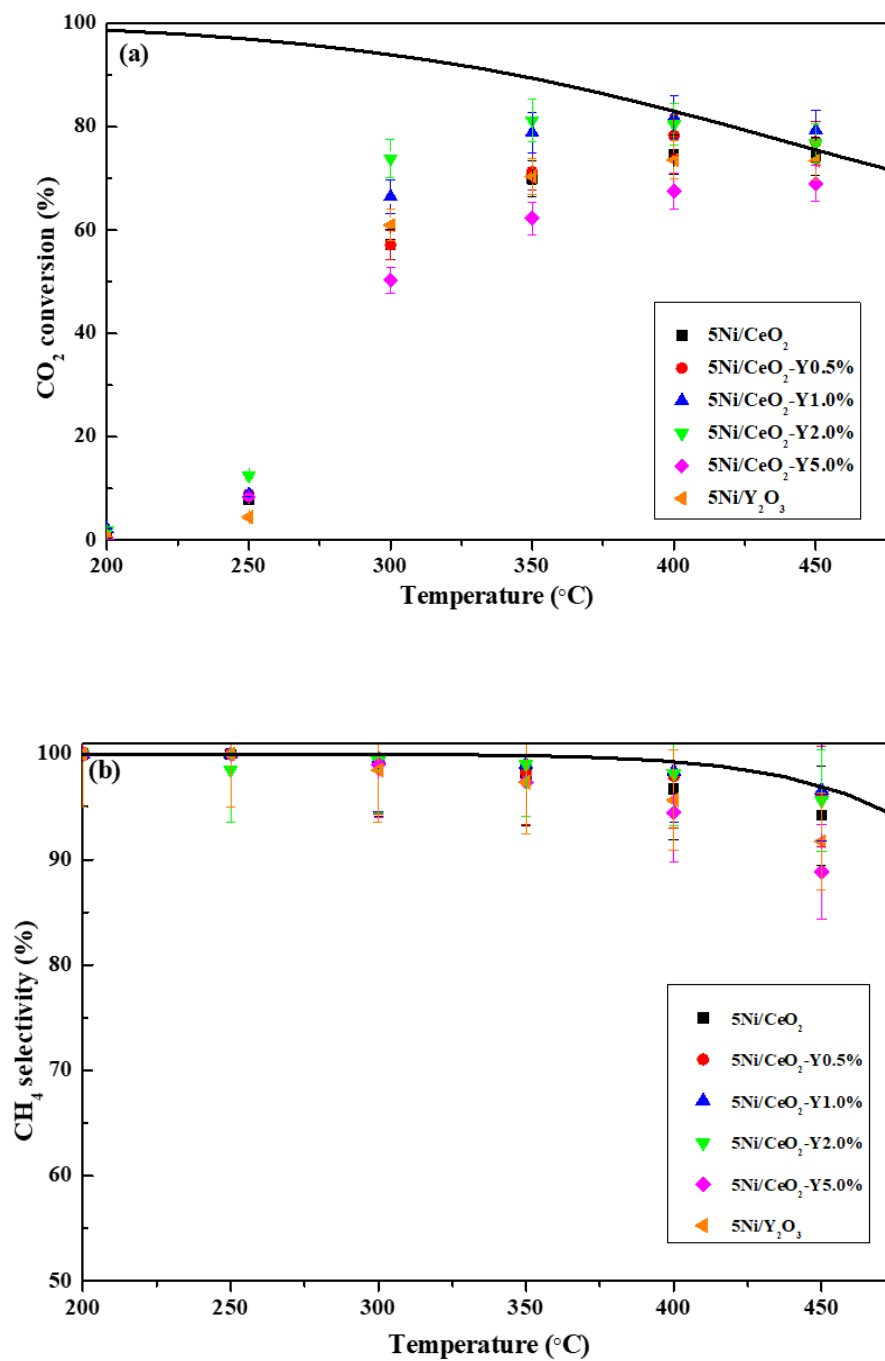


Figure. 5.13. Catalytic performances in methanation reaction as function of the temperature over the catalysts; (a) CO₂ conversion (b) CH₄ selectivity; Reaction conditions: WHSV=60,000 h⁻¹gcat⁻¹; CO₂/H₂/Ar=15/60/25; atmospheric pressure.

As shown in Fig. 5.13a, the highest CO₂ conversions for all the catalysts were obtained at 400 °C, which were close to the theoretic value, except for the sample of 5Ni/CeO₂-Y5.0%, which reached the highest conversion at 450 °C. In the temperature range of 250-350 °C, the CO₂ conversion for Y-modified catalysts gradually increased as the increase of yttrium up to 2 wt.% Y, afterward, the activity declined sharply when yttrium content reached 5 wt.%, which was less active than the 5Ni/Y₂O₃ catalyst. The 2 wt.% Y modified catalyst possessed the highest CO₂ conversion compared to the other catalysts at 250-350 °C. From Fig. 5.13b, it can be found that the CH₄ selectivity of all catalysts at low temperature (200-250 °C) appears very close to that of the theoretical value. Afterward, by further increase the temperatures up to 300-450 °C, the selectivity of all catalysts decreases gradually, and the worst value was obtained for 5Ni/CeO₂-Y5.0% and 5Ni/Y₂O₃ at a temperature higher than 400 °C.

In brief, the doping with yttrium into CeO₂ has a significant effect on the activity and selectivity of the Ni catalysts towards the Sabatier's reaction.

The Ni catalyst supported over CeO₂ modified by 2 wt.% Y possesses the best CO₂ conversion and high CH₄ selectivity at relatively low temperatures (i.e. 300-350 °C).

Table 5.7. The CO₂ methanation performance of the catalysts compared with the results reported in the references

Catalyst	GHSV/WSHV	Temperature (°C)	CO ₂ conversion (%)	CH ₄ selectivity	Reference
5Ni/CeO ₂	60,000 mL·g ⁻¹ h ⁻¹	350	69.9	98.1	This work
5Ni/CeO ₂ -Y2%	60,000 mL·g ⁻¹ h ⁻¹	350	81.2	99.1	This work
10Ni/CeO ₂	22,000 mL·g ⁻¹ h ⁻¹	340	91.1	-	[376]
5Ni/CeO ₂ -ZrO ₂ -AE	20, 000 mL·g ⁻¹ h ⁻¹ ₁	350	54.0	99.5	[377]
Ni/CeO ₂ (CT)	45,000 mL·g ⁻¹ h ⁻¹	340	91.1	100	[192]
Ni-CeO ₂ /SBA-15-V	60,000 mL·g ⁻¹ h ⁻¹	350	60.0	99.0	[224]
Ni-2CeO ₂ /Al ₂ O ₃	15,000 mL·g ⁻¹ h ⁻¹	350	85.0	100	[378]
15Ni/SBA-15-Op	10,000 mL·g ⁻¹ h ⁻¹	350	42	81	[171]
Ni/MCM-41	2,400 h ⁻¹	350	30	30	[346]
Ni/SiO ₂	2,400 h ⁻¹	350	58	58	[346]
Ni/Al ₂ O ₃	2,400 h ⁻¹	350	62	61	[346]
Ni/SBA-15	2,400 h ⁻¹	350	65	65	[346]
Ni/ZSM-5	2,400 h ⁻¹	350	70	70	[346]
Ni/ZrO ₂	4,8000 mL·g ⁻¹ h ⁻¹	350	80	99	[168]
Ni/La ₂ O ₃	20,000 kg ⁻¹ h ⁻¹	350	53	94	[198]

Ni/Sm ₂ O ₃	20,000 kg ⁻¹ h ⁻¹	350	70	97	[198]
Ni/CeO ₂	20,000 kg ⁻¹ h ⁻¹	350	73	97	[198]
Ni/Al ₂ O ₃	20,000 kg ⁻¹ h ⁻¹	350	75	99	[198]
Ni/ZrO ₂	20,000 kg ⁻¹ h ⁻¹	350	75	99	[198]
Ni/Y ₂ O ₃	20,000 kg ⁻¹ h ⁻¹	350	86	99	[198]
Ni/ZrO ₂ -P(DBD)	60,000 h ⁻¹	350	78	96	[136]
MO- 0.4Y(hydrotalcite derived)	12,000 h ⁻¹	350	89.1	99.2	[144]
Ni/Zr/CNT(carbon nanotube)	75,000 mL·g ⁻¹ h ⁻¹	350	40.0	96.0	[201]
Ni _{42.5} (hydrotalcite derived)	12,000 h ⁻¹	350	81.5	99.5	[131]
Ni ₂₁ La _{0.4} (hydrotalcite derived)	12,000 h ⁻¹	350	80.0	99.2	[206]
Ni ₂₀ Fe _{1.5} (hydrotalcite derived)	12,000 h ⁻¹	350	82	99	[205]

5.9 Relationships between physicochemical properties and catalytic performances

The mechanism of CO₂ methanation over Ni/CeO₂ catalysts has been studied in the literature [159,160]. It was attributed to the synergistic effect of two types of active sites, i.e. the active sites at the Ni-Ce-O interface for CO₂ adsorption and dissociation as well as the Ni⁰ sites for H₂ adsorption and dissociation. The H₂ dissociated to H- species on the surface of metallic nickel, and the CO₂ adsorbed on the surface of the support and then dissociated to carbonate or hydrogen carbonate species, then the carbonate or hydrogen carbonate were hydrogenated to formate species

including monodentate and bidentate formate. The monodentate formate could be hydrogenated to methane faster than the bidentate formate species. The larger is the metallic nickel surface area formed on catalyst by small Ni particles, the more favorable the adsorption and dissociation of H₂ are. The weak and medium basic sites were mainly useful for the dissociation of CO₂ in the reaction [160].

As shown in Fig. 5.14 (a, b and c), good relations were found at increasing Y loading between CO₂ conversion at 300 °C and the number of basic sites (weak + medium) (μmol/g_{cat}) (Fig. 5.14a) as well as between CO₂ conversion at 300 °C and the oxygen vacancies content, V₀ (%) (see Table 5.4) (Fig. 5.14b). A similar trend, at increasing Y loading, was observed between CO₂ conversion at 300 °C and the temperatures of β reduction peak that is related to the strength of the metal-support interaction of Ni over CeO₂-Y catalysts.

The CO₂ conversion at 300 °C was chosen for comparison because at low temperature (<300 °C) the results of CO₂ conversion were not very distinguishing. Meanwhile, the CO₂ conversion of all catalysts increases with the increase of temperature (350-450 °C, Fig. 5.13), which also makes the difference of catalytic performance unnoticeable. Thus, the 300 °C can be an appropriate temperature for comparison.

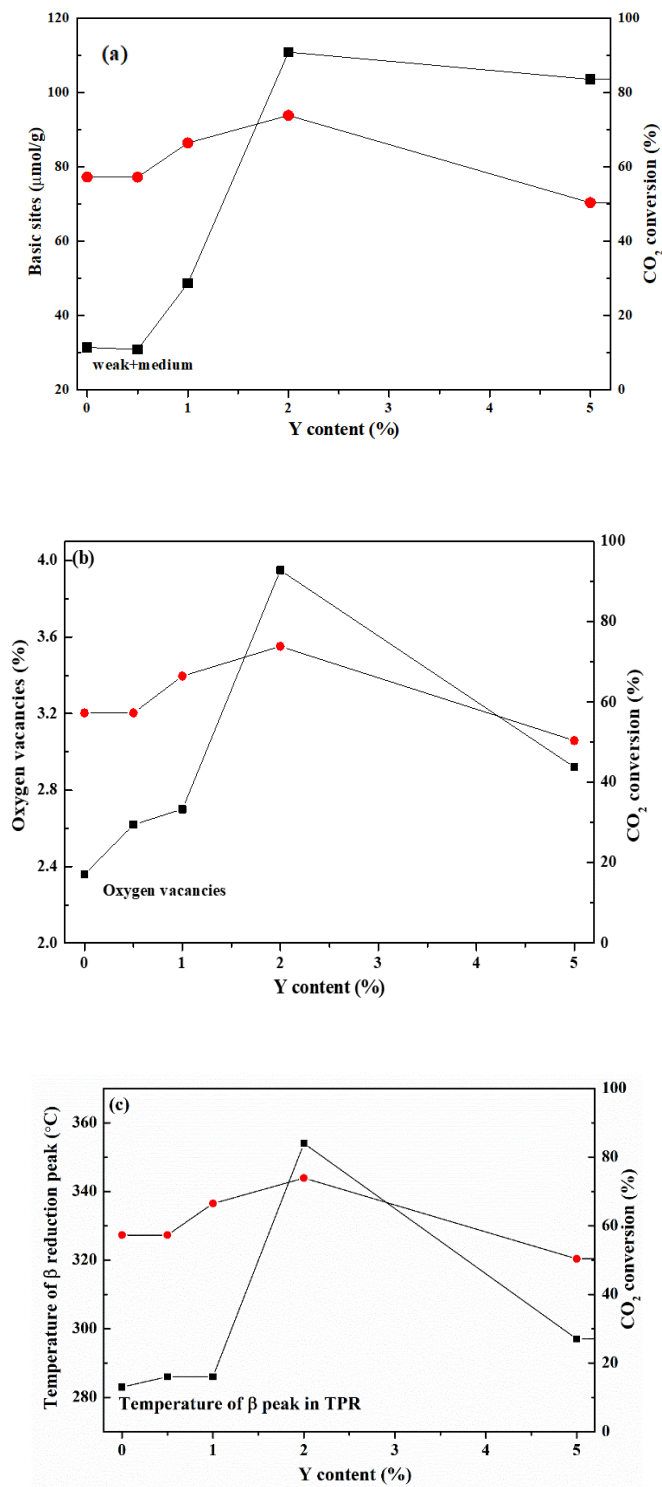


Figure. 5.14. Correlation of CO₂ conversion (at 300 °C) with (a) basic sites; (b) oxygen vacancies content, V_o (%); (c) temperature of β reduction peak in the TPR. The Y content represents the loading of Y for Ni/CeO₂-Y catalysts, with 0% representing 5Ni/CeO₂

So, based on the reported data and in agreement with the methanation reaction mechanism previously mentioned [159,160], it can be concluded that the decrease of CeO₂ particles, the high dispersion of nickel as well as the formation of more oxygen vacancies provide more active sites for the adsorption and dissociation of hydrogen and CO₂. Moreover, the high metal-support interaction depresses the sintering of active metal. For the 5Ni/CeO₂-Y2.0% sample, highly dispersed nickel particles provide more active sites for the adsorption and dissociation of hydrogen, the highest number of oxygen vacancies favors the adsorption of CO₂ and the highest amount of medium basic sites promotes the formation of monodentate formate, which can be fast hydrogenated to methane [160]. Thus, the highest CO₂ conversion and relatively high CH₄ selectivity were obtained on the catalyst.

5.10 Steady-state test of Ni/CeO₂ based catalysts in CO₂ methanation

The steady-state tests were performed on three selected Ni catalysts, by using the same set-up previously described in Chapter 3, for evaluating the stability of CO₂ conversion and selectivity towards CH₄. In a typical process, 100 mg of calcined sample was loaded into the reactor. After reduction, the sample was cooled down to 300 °C, then the gas mixture with molar ratio CO₂/H₂/Ar=15/60/25 (100 mL/min) was fed into the catalyst (WHSV=60,000 mL h⁻¹g_{cat}⁻¹). The products were analyzed by the TCD detector in GC (490 Varian, Agilent). The experiment was maintained at 300 °C for 7 h. 5Ni/CeO₂-Y1.0% and 5Ni/CeO₂-Y2.0% were selected for steady-state tests at 300 °C for 7h. The temperature of 300 °C was selected due to the recognizable difference of CO₂ conversion values shown in Fig. 5.13. The 5Ni/CeO₂ sample was used for comparison. The selected catalysts were reduced in the same condition as for the CO₂ methanation test, then were cooled down to 300 °C and the reaction gas mixture was fed into the reactor. The

steady-state test results are displayed in Fig. 5.15. It can be seen from Fig. 5.15a that the CO₂ conversion values of all samples decrease slightly at the beginning, then keep stable on stream. Both Y-promoted catalysts performed better than Ni/CeO₂, with 5Ni/CeO₂-Y2.0% showing the best CO₂ conversion. The results of 5Ni/CeO₂ were slightly higher than those shown in Fig. 5.13a. This was attributed to possible effects, within the experimental error of 5%, during the catalytic tests. The selectivity to CH₄ is shown in Fig. 5.15b, the values maintain nearly stable during the test and both Y-modified catalysts achieved higher selectivity than Ni/CeO₂ catalyst.

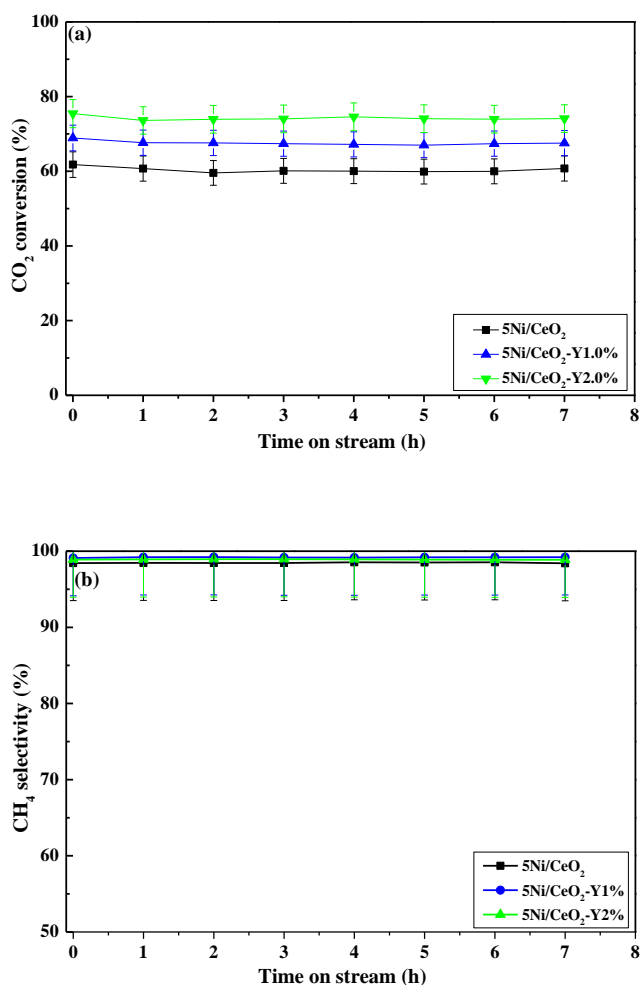


Figure. 5.15. CO₂ methanation stabilities over 5Ni/CeO₂, 5Ni/CeO₂-Y1.0% and 5Ni/CeO₂-Y2.0% catalysts (a) CO₂ conversion with error bars; (b) CH₄ selectivity; Reaction condition: temperature 300 °C, WHSV=60,000 h⁻¹g_{cat}⁻¹, reaction gas mixture CO₂/H₂/Ar=15/60/25.

The slight difference in the conversions (lower than 3%) in between catalytic tests from 200 °C to 450 °C and steady-state experiments can be explained by the fact that, in the former case, the catalysts were exposed to a lower temperature (250°C) for at least 30 min, as described in the experimental part, before reaching 300°C.

5.11 Characterization of Ni/CeO₂ based catalysts after steady-state test

5.11.1 XRD patterns of the catalysts after steady-state test

To investigate structural modifications of the catalysts after the steady-state test, XRD patterns were registered and are shown in Fig. 5.16. No diffraction peaks of metallic nickel or NiO were found, meaning that the nickel species remained highly dispersed on the support even after a steady-state test at 300 °C for 7h. This finding confirms the XRD results of the catalysts after the activity test. A perusal of Fig 5.16b (enlarged pattern in the range between 42 and 52° 2 θ) shows a slight shift to higher angles of all CeO₂ and CeO₂-Y peaks in comparison with Fig 5.2a, especially in the case of 5Ni/CeO₂-Y2.0%, in which the (202) peak is centered at 47.65° 2 θ . This finding would point to further inward diffusion of Y³⁺ and Ni²⁺ into the ceria lattice, as suggested by the XPS analysis (see Table 5.9). In Table 5.8 the particle sizes of CeO₂ support calculated by the Debye-Scherrer equation are listed. The values are in good agreement with those given in Table 5.2, remarking that no sintering of ceria nanoclusters takes place at 300 °C under the reaction stream. The 5Ni/CeO₂-Y2.0% maintained the smallest particle size of ceria. Such results account for the good stability in CO₂ conversion and CH₄ selectivity registered being the sintering of active metals the main reason for deactivation in Sabatier's reaction [192].

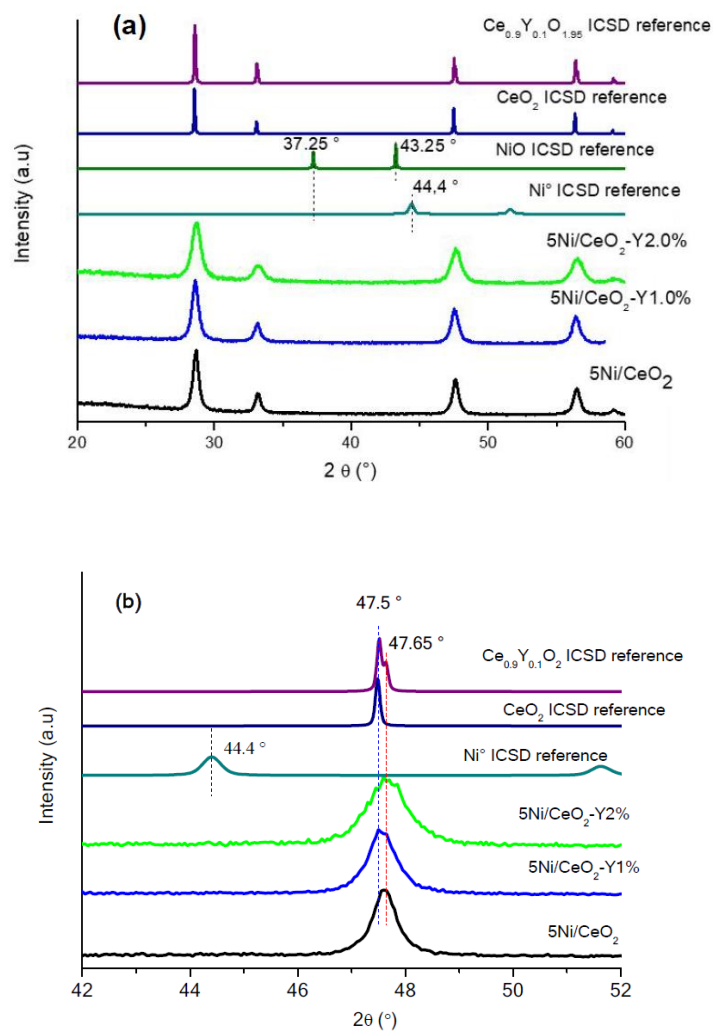


Figure. 5.16. XRD pattern of the catalysts after steady-state test; Condition: After the steady-state test, the samples were cooled down to ambient temperature under pure He flow (100 mL/min)

Table 5.8 The CeO₂ particle sizes of catalysts after steady-state test

Catalyst	Particle size of CeO ₂ ^a (nm)
5Ni/CeO ₂	17.3
5Ni/CeO ₂ -Y1.0%	16.0
5Ni/CeO ₂ -Y2.0%	12.1

^a Calculated by Debye-Scherrer equation fitting the 4 strongest peaks in XRD patterns.

5.11.2 XPS analysis of the catalysts after steady-state test

To obtain the surface composition and oxidation states of the catalysts after a steady test, the XPS analyses of the spent catalysts were performed. The Ce3d, Ni2p, and O1s XPS regions of the samples are displayed in Fig. 5.17, respectively. The surface oxidation state, atomic ratio, and binding energies are shown in Table 5.9. As already shown in Fig. 5.1.4, the Ce3d spectra were fitted with 10 peaks, in which four peaks are attributed to Ce (III) and six peaks are attributed to Ce (IV). Because of the small dimension of the nickel particles, surface re-oxidation occurs after catalytic reaction, likely during exposure to the atmosphere, so it was impossible to calculate the degree of nickel reduction.

Compared to the XPS results of calcined samples (Table 5.3), a small decrease in the Ni/Ce ratio was found (Table 5.9). Conversely, the Y/Ce ratio decreased by an important extent, indicating a probable migration of yttrium into the bulk during steady-state reaction.

The Ce (III) % of the samples nearly keep the same value as those of calcined samples, meaning that the surface Ce³⁺ species of the catalysts were oxidized during the test, while the values (%) of OOH decreased a little in comparison with those of the calcined samples, indicating decreased oxygen vacancies because of the occurrence of reoxidation. A decrease of the Ni/Ce ratio and a simultaneous shift of Ni2p_{3/2} peak at higher energies suggest a small increase of Ni particles size after the steady-state test and different interactions with the support.

As previously stated for calcined samples, there is no significant difference regarding the binding energy of Y3d_{5/2}.

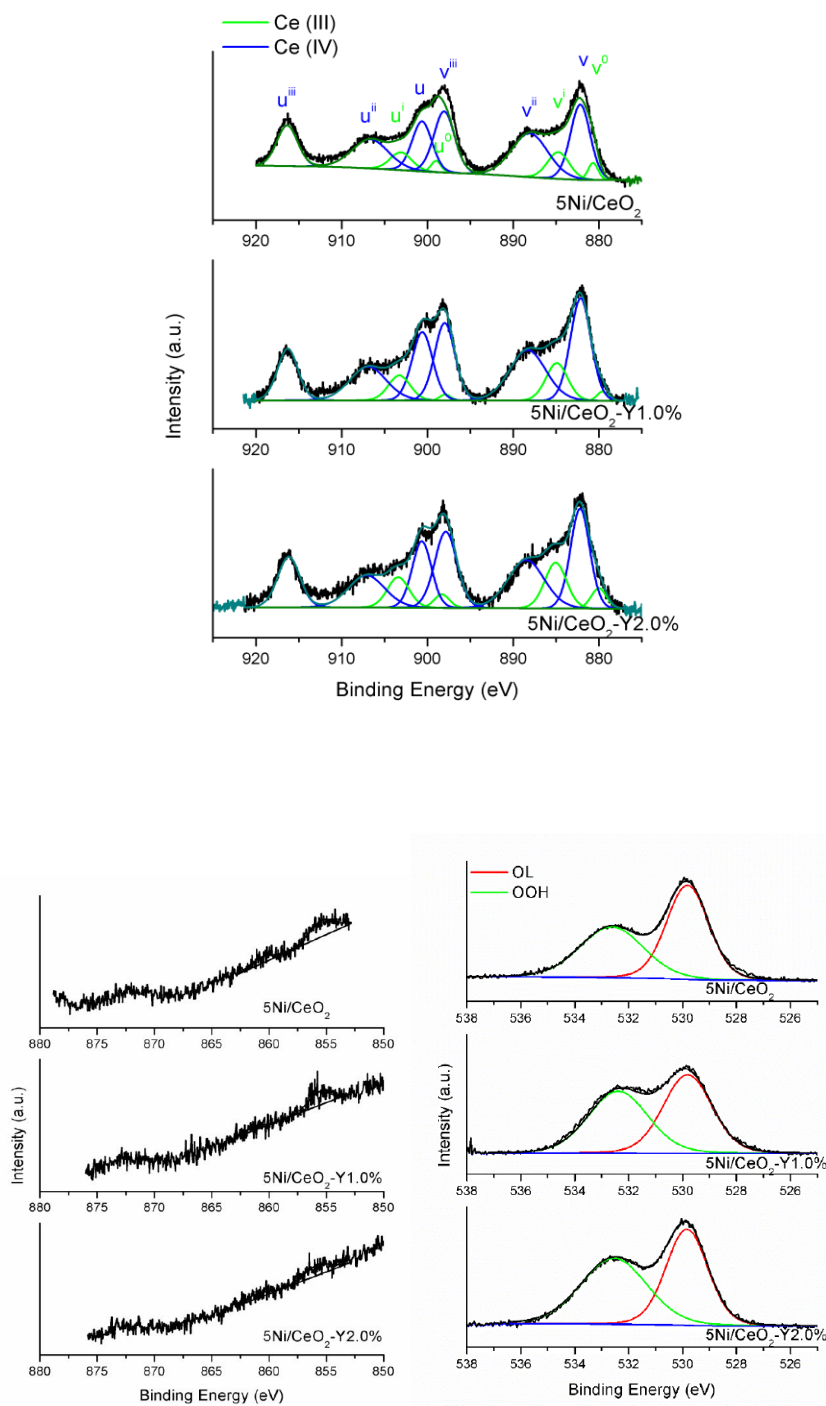


Figure. 5.17. The XPS Ce3d, Ni2p, and O1s spectra of the samples after steady-state test; Steady-state test: 300 °C for 7 h in methanation reaction

Table 5.9 XPS derived Ce (III) and Ce (IV) percentage, Binding Energy of O1s, Ni2p_{3/2} and Y3d_{5/2} in eV, Ni/Ce and Y/Ce atomic ratio for the samples after the steady-state test. In parenthesis, the relative percentage between OL and OOH is indicated.

Catalyst	Ce(III)- Ce(IV)	O1s (eV)		Ni2p _{3/2} (eV)	Ni/Ce	Y3d _{5/2} (eV)	Y/Ce
		OL	OOH				
5Ni/CeO ₂	11%-89%	529.9 (53%)	532.8 (47%)	855.3	0.18	-	-
5Ni/CeO ₂ -Y1.0%	11%-89%	529.9 (47%)	532.6 (53%)	855.6	0.16	157.8	0.38
5Ni/CeO ₂ -Y2.0%	16%-84%	530.1 (49%)	532.2 (41%)	855.7	0.16	158.2	0.42

5.12. Conclusions and perspectives

Y-modified CeO₂ oxides have been successfully synthesized by the hydrothermal method and used as supports for Ni deposition by wetness impregnation. The catalytic performances were investigated in CO₂ methanation reaction and are discussed in line with Physico-chemical characterizations of calcined, reduced, and spent catalysts. It has been proven that such Ni catalysts with proper Y loadings are suitable catalysts for CO₂ methanation reaction between 250-350 °C with high selectivity towards methane formation.

The specific surface area of Ni/CeO₂-Y samples, the crystallite sizes of ceria, the oxygen vacancies content, and the interaction between NiO and CeO₂ can be tuned by different Y content as shown by N₂ adsorption/desorption, XRD, XPS, TPR, TEM, HR-TEM, TGA, CO₂ TPD. All the catalysts contain well-defined crystallites and the introduction of Y tailors the particle sizes and shapes of CeO₂ in the catalysts. Unpromoted CeO₂ particles are large nano-cubes turning to nanorods by Y promotion, with an increase of these nanorods size of up to 2 wt% of Y addition.

Highly dispersed Ni active sites in strong interaction with the ceria-based oxide and the oxygen vacancies formed by Y addition are the key factors determining high catalytic activity and stable performances of the Ni/CeO₂-Y catalysts.

The Ni/CeO₂-Y 2.0% with the highest number of oxygen vacancies able to activate CO₂ and with the strongest metal-support interaction suppressing sintering of the Ni sites for H₂ activation, was the best performing CO₂ methanation catalyst.

CeO₂ is highly active support for Ni catalysts and Y is a good promoter to improve Ni/CeO₂ catalyst in CO₂ methanation. Besides, CeO₂ and Y₂O₃ can also be good supports or promoters for Ni catalysts. Thus, the effects of such promoters in Ni catalysts supported on mesoporous materials are presented in the next chapter.



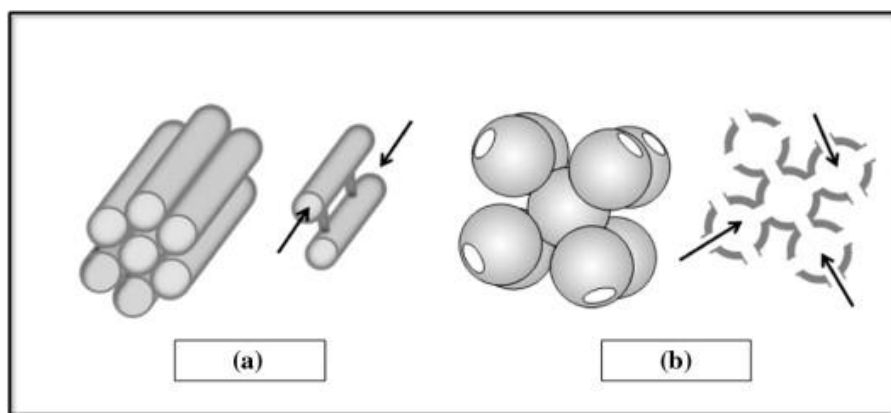
Chapter VI

Ordered mesoporous silica supported Ni catalysts for CO₂ methanation

6. Ordered mesoporous silica supported Ni catalysts for CO₂ methanation

6.1. Introduction

In this section, two types of highly ordered mesoporous silicas are presented. SBA-15 (Santa Barbara Amorphous), which was developed by Zhao et al. [379], was synthesized and used to prepare Ni catalysts for CO₂ methanation. SBA-15 has a two-dimensional $p6mm$ hexagonal structure, with a well-ordered hexagonal array and one-dimensional channel structure as shown in Figure. 6.1 [379]. SBA-16, developed by the same team [379], was also synthesized and employed in Ni catalysts preparation. On the contrary, SBA16 has a three-dimensional cubic cage-like structure with an ultra-large cell parameter (Shown in Figure. 6.2) [252,380,381].



Scheme 6.1. Schematic illustration of the meso-channels of SBA-15 (a) and nano cage-like of SBA-16 (b). Adapted from [382].

As shown in Scheme 6.1, SBA-15 and SBA-16 have very distinctive structures. SBA-15 displays parallel pores and highly ordered hexagonal arrangement [382]. Meanwhile, SBA-16 possesses body-centered cage-like pores with cubic arrangement [382]. Considering the structure properties

of SBA-15 and SBA-16, they would be interesting materials in catalysis. Some reports have applied such materials in various CO₂ utilization reactions as shown in Table 6.1. Given the results above, mesoporous silica (SBA-15 and SBA-16) can be interesting to Ni catalysts in CO₂ methanation.

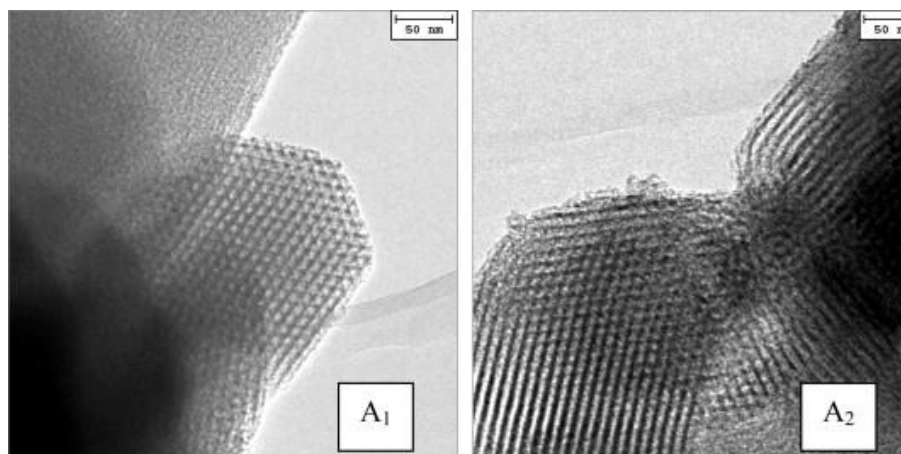


Figure. 6.1. The hexagonal structure and ordered channels of SBA-15. Adapted from [382]

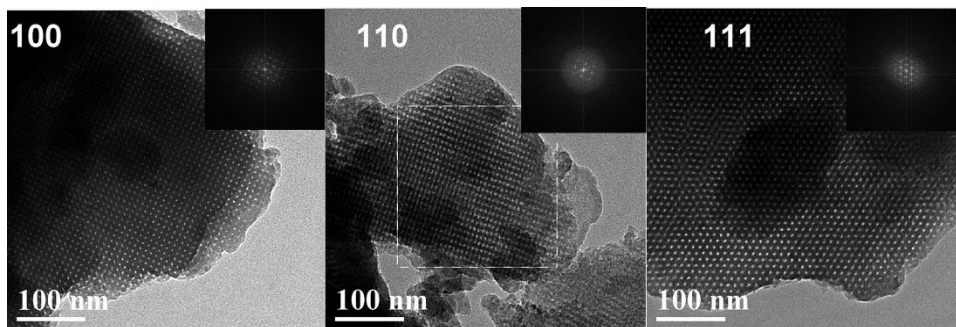


Figure. 6.2. Diffractograms along with different projections of the *Im3m* structure of SBA-16. Adapted from [380].

Table 6.1 The SBA-15 and SBA-16 utilized in various CO₂ utilization reactions

Catalyst	Reaction	Reference
Ni/SBA-15	dry reforming of methane	[383]
Ni/Ce-SBA-15	dry reforming of methane	[384]
Ni/CeZr/SBA-15	dry reforming of methane	[385]
Ni/TiN-SBA-15	dry reforming of methane	[386]
Co-Ni/Sc-SBA-15	dry reforming of methane	[387]
Ni/Ce/SBA-15	CO ₂ methanation	[178]
Ni-Mg/SBA-15	CO ₂ methanation	[179]
Ni-La ₂ O ₃ /SBA-15	CO ₂ methanation	[169]
Ni-Y/SBA-16	Cyclic Chemical Looping Steam Methane Reforming	[388]
Ni-Ce/SBA-16	dry reforming of methane	[389]
Ni-Mg/SBA-16	dry reforming of methane	[390]
Ni/SBA-16	CO ₂ methanation	[204]
Ni/SBA-16	CO ₂ methanation	[182]

Thus, in this chapter, we will present first a study on SBA-15 supported catalysts doped by Ce and Y. Furthermore, Ni catalysts supported on SBA-16 are also presented.

6.2. SBA-15 supported Ni catalysts doped by Y and Ce

6.2.1 Introduction

Oxide materials such as CeO₂ [137], ZrO₂ [201], Al₂O₃ [214,275], hydrotalcite [144,391], SiO₂ [161], etc. had received intensive research interests. In chapter 4 and 5, the low-cost materials and CeO₂ were investigated. Meanwhile, the ordered mesoporous materials like SBA-15 [171,179,221,224], MCM-41 [221,392,393], KIT-6 [50], and SBA-16 [142,204], have also been used as supports for the preparation of Ni catalysts thanks to their unique properties. Among

mesoporous silicas, Santa Barbara Amorphous-15 (SBA-15) has attracted significant attention due to its high specific surface area (up to 1160 m²/g), particular pore size distribution (50-300 Å), large pore volume (up to 2.5 cm³/g), well-ordered pore structure, and high thermal stability [66]. The highly ordered structure can limit the sintering of Ni particles at high temperatures, whereas an enhanced specific surface area and high pore volume contribute to the high dispersion of Ni active sites. SBA-15 has been extensively used as support for the preparation of Ni/SBA-15 catalysts. Liu et al. [171] synthesized Ni/SBA-15 catalysts by one-pot hydrothermal method (Ni/SBA-15-op) and conventional impregnation method (Ni/SBA-15-Im), investigating their catalytic performance in CO₂ methanation. It was found that Ni/SBA-15-op catalyst was more active than Ni/SBA-15-Im due to higher surface area, larger pore volume, and enhanced dispersion of nickel particles in Ni/SBA-15-op. Furthermore, the addition of promoters to Ni catalysts can significantly contribute to an improvement in catalytic efficiency. Bian et al. [178] synthesized the Ni/SBA-15 and Ni/Ce/SBA-15 catalysts by the sequential impregnation method and the dried Ni/Ce/SBA-15 (nitrate nickel) samples were processed by dielectric barrier discharge (DBD) plasma and calcination in air. It was found that the Ce addition to Ni/SBA-15 significantly improved the activity and selectivity of the catalyst, regardless of the calcination or DBD plasma process. After modification with ceria, the catalyst decomposed by plasma (Ni/Ce/SBA-15-P) performed the best activity, which was attributed to the high dispersion of Ni, better reducibility, and increased number of basic sites. Apart from the process of plasma decomposition, Ni/Ce/SBA-15 catalysts calcined in air or vacuum were also reported in CO₂ methanation [224]. The study illustrated that the catalyst obtained under vacuum thermal treatment (Ni-CeO₂/SBA-15-V) showed better activity and selectivity compared to those thermally treated in the air (Ni-

CeO₂/SBA-15-air). This was attributed to the smaller particle size of Ni and CeO₂, as well as highly dispersed Ni species, being in close vicinity to Ce.

Other promoters, such as Zr [394,395], Ce_xZr_{1-x}O₂ [396], Y [64], Mg [179,397] were also used to enhance performance of Ni/SBA-15 catalysts in various catalytic reactions. Cerium and zirconium were commonly applied to improve nickel-based catalysts due to their redox and oxygen storage abilities. In chapter 5, the modification with Y on the catalytic performance of Ni/CeO₂ in CO₂ methanation was studied [141]. It found that the incorporation of yttrium could substantially promote the activity of Ni/CeO₂. The positive effect of yttrium was assigned to the existence of smaller CeO₂ crystal size, increased BET surface area, enhanced Ni-Ce metal-support interaction, and the increased oxygen vacancies for Y-doped Ni/CeO₂ catalysts.

Compared to the Ni catalysts promoted by one additive, the promotion with Ce-Zr or Ce-Y dual additives of Ni-based mesoporous catalysts have been studied on reactions, such as CO methanation and dry reforming of methane, which showed better performance in such reactions [385,398]. However, only a few studies focused on the Ni/SBA-15 catalyst modified by two promoters in CO₂ methanation. Considering the benefits of CeO₂ and Y₂O₃, here we investigated the effects of Ce and Y on the performances of SBA-15 supported Ni catalysts in CO₂ methanation. Ni/SBA-15 catalysts with a fixed content of Ce (10 wt.%) and different loadings of Y (2, 4, 10 wt.%) were synthesized by co-impregnation method and characterized by a variety of techniques, such as N₂ physisorption, small-angle X-ray scattering (SAXS), X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), H₂ temperature-programmed reduction (H₂-TPR), CO₂ temperature-programmed desorption (CO₂-TPD), H₂ chemisorption, and thermogravimetric analysis coupled with mass spectrometry (TGA-MS). This study aims to investigate the influence of Y on NiCe/SBA-15 catalysts in CO₂

methanation. The yttrium individually doped Ni/SBA-15 catalysts were also synthesized and tested in CO₂ methanation as a comparison.

6.2.2 Catalysts preparation and characterization

The synthesis procedures of SBA-15 and subsequent supported Ni catalysts were introduced in 3.1.4 (Chapter 3). Characterization techniques were shown in 3.3 (Chapter 3).

6.2.3 Textural properties, structural parameters, metal distribution, and chemical surface composition of the studied catalysts

The textural properties of the calcined samples were measured by N₂ physisorption. N₂ isotherms and pore size distributions are presented in Fig. 6.3. As shown in Fig. 6.3a, all samples with and without yttrium showed type IV isotherm with H1 hysteresis loop, clearly demonstrating the presence of mesoporous feature [399]. The parallel adsorption and desorption curves also indicate highly ordered cylindrical channels present in the samples. This shows that the ordered 2D structure was preserved after modification with promoters. With the increasing yttrium loading, the inflection step slightly shifts towards lower relative pressure (p/p_0), indicating a slight reduction of ordered mesopores [179]. The specific surface area (SSA), pore volume (V_p), and average pore width (D_{ap}) are presented in Table 6.2. In this study, SSA and V_p of the studied Ni/SBA-15 catalysts are similar to those described in other reports on Ni/SBA-15 catalysts [400,401]. Despite a significant decrease of SSA observed for the Ce-promoted samples, the obtained values are still high and comparable to those reported elsewhere [61,64,385]. This can be attributed to a cluster formation or deposition of promoter clogging the porous channels of the

support [385]. Moreover, this indicates that the surfactant CTAB, added in the preparation step, can be a suitable reagent used during the synthesis of Ni/SBA-15 catalysts. Furthermore, the presence of yttrium can positively influence the textural properties [141,144]. As presented in Table 6.2, SSA and V_p were higher when 4 wt.% of Y was used. Then, both SSA and V_p decreased for the sample containing 10 wt.% of Y loading. Fig. 6.3b depicts BJH pore size distribution measured for the studied catalysts. It can be seen that the pore size of all the samples mainly locates in the range of 2-8 nm. It can be seen that metal oxides (Ni and Ce) deposited onto the SBA-15 support resulted in a decrease of average pore size from 6.8 nm for SBA-15 to 6.2 nm for 15Ni10Ce/SBA-15. Moreover, the Y addition led to a slight decrease of average pore size from 6.2 nm to 5.9 nm for 15Ni10Ce/SBA-15 and 15Ni10Ce10Y/SBA-15, respectively. This can be linked with an effect of the deposition of metal oxides inside the mesopores, which was also found for La-promoted Ni/SBA-15 catalyst [169]. One can note that the appropriate loading of Y (4 wt.%) led to an increase of specific surface area and pore volume in Ce-Y-promoted Ni/SBA-15 catalysts. Similar observations were found by Świrk et al.[49] for yttrium promoted Ni/Mg/Al hydrotalcite-derived mixed oxides. Among the yttrium modified samples with 3, 4 and 8 wt.%, NiY4-DLH revealed the highest specific surface area.

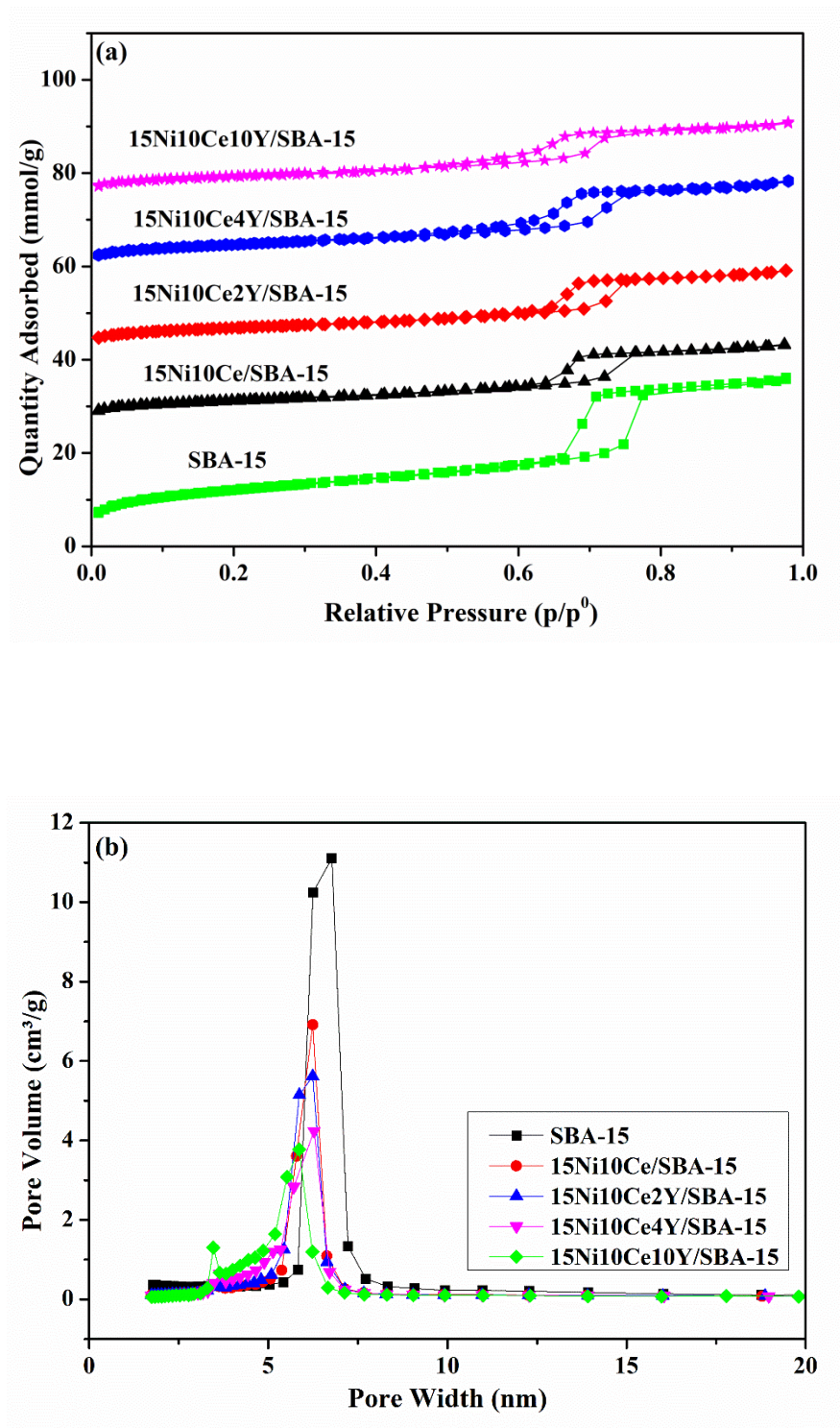


Figure. 6.3. N₂ adsorption-desorption isotherms a) and the BJH pore width distribution b) of the calcined catalysts. For clarity, the isotherms were vertically shifted.

The ordered structure of the calcined SBA-15, 15Ni10Ce/SBA-15, and 15Ni10Ce10Y/SBA-15 were studied by Small-angle X-ray diffraction. Three peaks between $2\theta = 0.5$ – 4° were registered for all samples with the most intense at $2\theta = 0.9^\circ$ and two well-resolved at 2θ of ca. 1.5° , and 1.8° corresponding to (100) (110) and (200) crystal planes, respectively. Their presence is attributed to the highly ordered 2D hexagonal structure (*p6mm*) which is a typical structure for SBA-15 [251,402]. This shows that the co-impregnation with Ni, Ce, and Y allows maintaining the ordered mesoporous structure of SBA-15 catalysts, however, their peaks shifted toward higher angles (Fig. 6.4) as the unit cell parameter decreased after modification with metals (Table 6.2). The calculated values are in the range of 11.2–11.9 nm, being in good agreement with those estimated in other literature reports [402,403]. The recorded decrease in unit cell parameter suggests that nickel, cerium, and yttrium species were partially deposited on the outer surface of SBA-15 support [251,404]. As presented in Fig. 6.4, the intensity of the diffraction peaks gradually decreased after modifications with Ni-Ce and Ni-Ce-Y. This can be explained by partial destruction of the pore structure orderliness of 15Ni10Ce/SBA-15 and 15Ni10Ce10Y/SBA-15 catalysts [169,405].

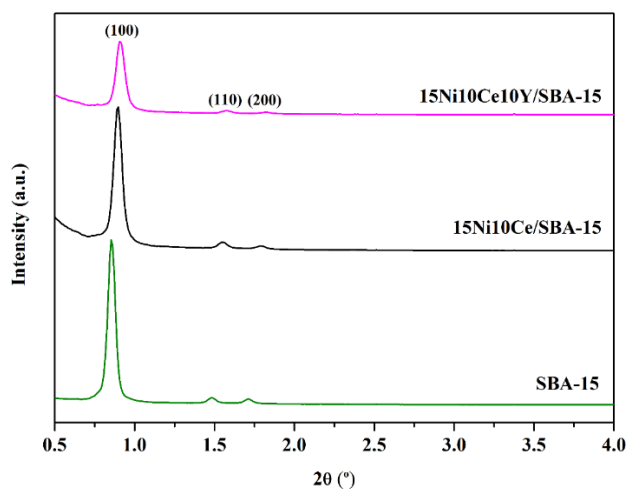


Figure. 6.4. Small-angle X-ray diffraction patterns of the calcined SBA-15, 15Ni10Ce/SBA-15 and 15Ni10Ce10Y/SBA-15.

The structural properties of the calcined and reduced catalysts were characterized by wide-angle X-ray diffraction and the recorded patterns are depicted in Fig. 6.5. As shown in Fig. 6.5a, the diffraction peaks at $2\theta=37.1, 43.1, 62.7, 75.2,$ and 79.3° were registered for all samples, which were assigned to the presence of cubic NiO, corresponding to the (111), (200), (220), (311) and (222) planes, respectively [406,407]. For the calcined 15Ni10Ce/SBA-15 sample, only NiO was registered as a segregate phase. No separate phase of cerium species was observed which may indicate their high dispersion. By increasing the Y loading, small diffraction peaks located at 28.9° and 33.1° appeared for the 15Ni10Ce10Y/SBA-15 sample, which may suggest the existence of Y₂O₃ (ICSD reference no. 193377) and CeO₂ (ICSD reference no. 28753), respectively [141]. The modification with Y loading of 10 wt.% may lead to a slight decrease of the dispersion of yttria and ceria on the SBA-15 support due to the deposition of the metal species on the outer surface [51].

By increasing the yttrium loading, a small shift of the diffraction peak of NiO was identified for Y and Ce modified samples. The diffraction peaks located at 37.08 and 43.11° on the 15Ni10Ce/SBA-15 sample shifted to 37.27 and 43.34° for 15Ni10Ce10Y/SBA-15, indicating that the partial introduction of Ni²⁺ into CeO₂ lattice may occur [141]. For the 15Ni10Ce10Y/SBA-15 sample, apart from the possible reflection of Y₂O₃, the diffraction peaks centered at 28.56 and 28.55° possibly arising from CeO₂ (ICSD reference no. 28753) and Ce-Y solid solution (ICSD reference no. 28808, cubic, space group $Fm\bar{3}m$), respectively, cannot be excluded because of their adjacent positions. Hence, it can be speculated that the solid solution of Y-Ce can be formed on yttrium and cerium containing samples. The formation of Y-Ce solid solution can be formed by the similar ion radius of Ce⁴⁺ (0.97 \AA) and the Y³⁺ dopant (1.02 \AA), which led to the replacement of Ce by Y in the lattice [408]. This may be demonstrated by subsequent XPS results.

Table 6.2. The textural properties, the crystallite size of NiO, and metallic Ni measured for the reduced samples.

Catalyst	SSA (m ² /g) ^a	V _p (cm ³ /g) ^b	Crystallite size (nm) ^c		Crystallite size of Ni ^o (nm) ^d	Dispersion of Ni (%) ^d	Lattice Parameter <i>a</i> (nm) ^e
			NiO	Ni ⁰			
SBA-15	973	1.09	n/p	n/p	n/p	n/p	11.9
15Ni10Ce/SBA-15	400	0.54	13	20	11.0	3.2	11.4
15Ni10Ce2Y/SBA-15	410	0.55	14	22	12.1	3.1	n/m
15Ni10Ce4Y/SBA-15	443	0.61	15	17	12.5	3.1	n/m
15Ni10Ce10Y/SBA-15	395	0.53	15	21	11.4	3.4	11.2

n/p: not present. n/m: not measured

^a Calculated by a BET calculation method.^b Calculated by BJH desorption method.^c Calculated from XRD by the Scherrer equation.^d Calculated by H₂ chemisorption assuming spherical nickel crystallites of uniform size.^e Calculated from SAXS by $a=2d_{(100)}/\sqrt{3}$

Wide-angle XRD patterns of the reduced catalysts are depicted in Fig. 6.5b. The structural properties of the catalysts changed after reduction compared to the calcined samples. Only three peaks located at $2\theta=44.69^\circ$, 52.03° , and 76.60° were registered, which were assigned to the diffraction of metallic Ni, corresponding to (111), (200), and (220) planes, respectively [204]. The peak positioned at $2\theta=28.60^\circ$ was too weak to be identified, meaning the dispersion of yttria or ceria was improved after reduction. Similar to the calcined samples, a slight shift of the reflection from $2\theta=44.69^\circ$ for 15Ni10Ce/SBA-15 to $2\theta=44.56^\circ$ for 15Ni10Ce10Y/SBA-15 was found. Nevertheless, it is difficult to estimate whether the insertion of Ni into the Ce or Si structure occurred, as there was no clear diffraction peak of ceria, making the comparison of cell parameter impossible [409].

The crystallite size of NiO and Ni⁰ were calculated by the Scherrer equation and listed in Table 6.2. It can be seen that the introduction of Y did not have a significant effect on the crystal size of NiO or Ni metal. Meanwhile, the crystallite size of metallic Ni increased compared to the NiO calculated for the calcined materials, which can be attributed to the phase change during the reduction step.

H₂ chemisorption experiments were carried out and the dispersion of Ni, as well as the estimated size of Ni⁰ crystallites, are presented in Table 6.2. With the increasing Y loading up to 4 wt.%, the dispersion of Ni did not change significantly. Furthermore, there is no significant difference regarding the Ni⁰ particle size, indicating that the addition of Y has only a slight effect on active sites. The difference of Ni⁰ particle size obtained from different methods (XRD or H₂ chemisorption) can be attributed to the effect of different measurements or the not 100% reduction of nickel.

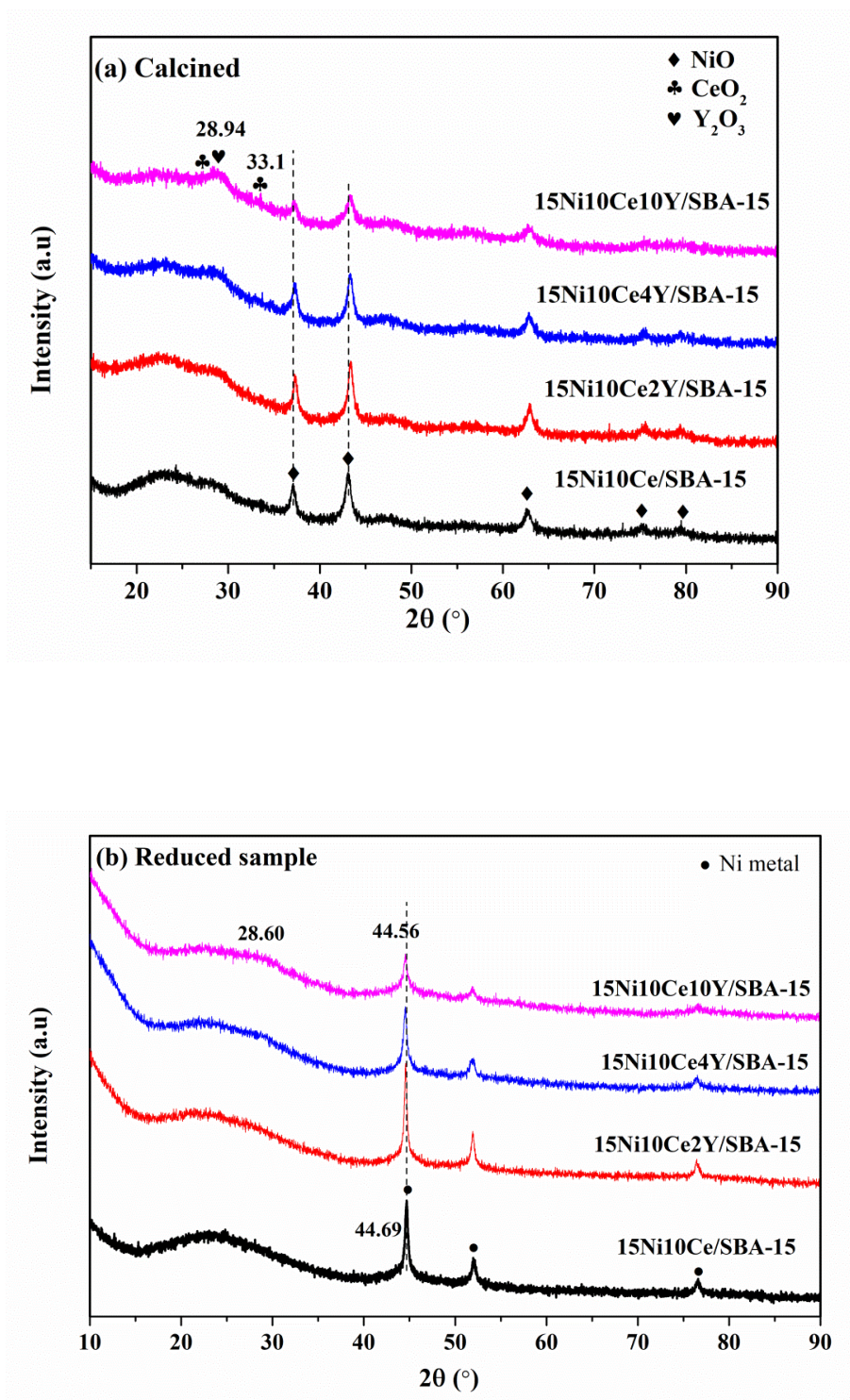


Figure. 6.5. XRD patterns of the catalysts promoted with cerium and cerium-yttrium; (a) calcined samples, (b) reduced samples

In order to confirm the unique structure of SBA-15 and to determine the dispersion of Y₂O₃, CeO₂, and Ni⁰ on the surface, the TEM and EDS analyses were conducted for the reduced catalysts. The micrographs are presented in Fig.6.6 with the preserved well-defined two-dimensional channels and the hexagonal pore arrangement. These results demonstrated that the distinct mesostructure was maintained after impregnation with metals. This result is consistent with the SAXS. Fig.6.6a shows micrographs of 15Ni10Ce/SBA-15 catalyst with big Ni particles that were probably formed by the agglomeration of nickel outside the mesoporous channels of SBA-15. On the contrary, 15Ni10Ce10Y/SBA-15 catalyst presented well-dispersed Ni species inside the channels of the support, with only a few big particles found on the outer surface (Fig. 6.6b).

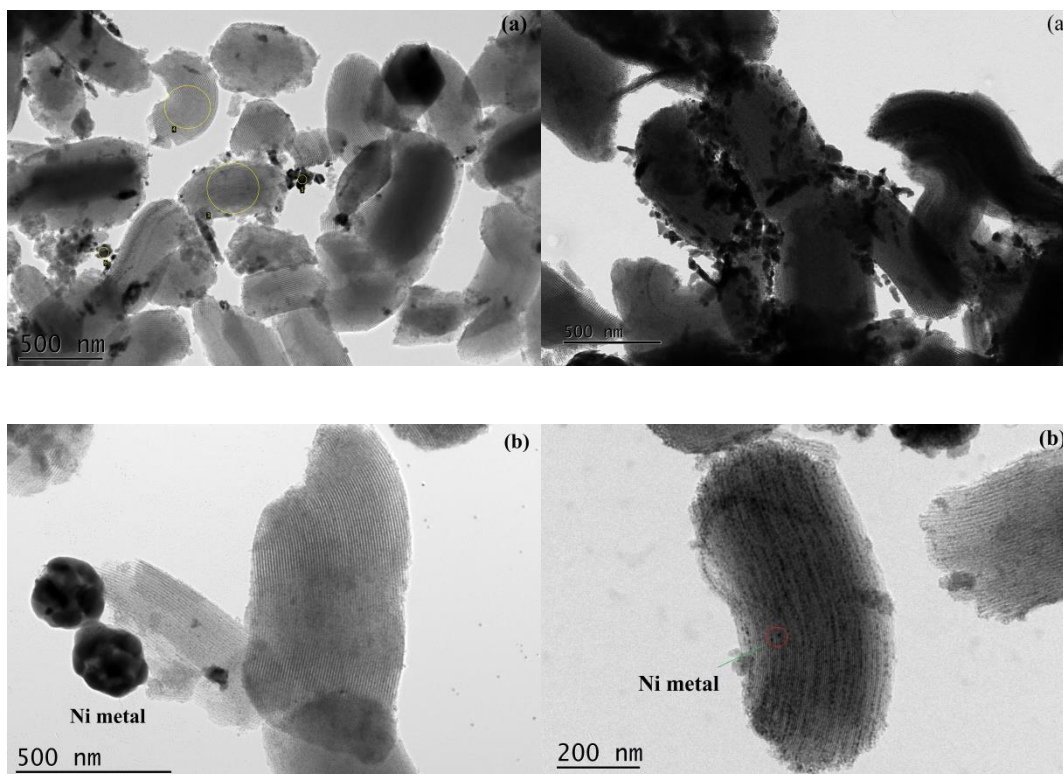


Figure. 6.6. TEM micrographs of the reduced catalysts; Conditions: 550 °C for 1.5h under 5%H₂/Ar; (a) 15Ni10Ce/SBA-15, (b) 15Ni10Ce10Y/SBA-15.

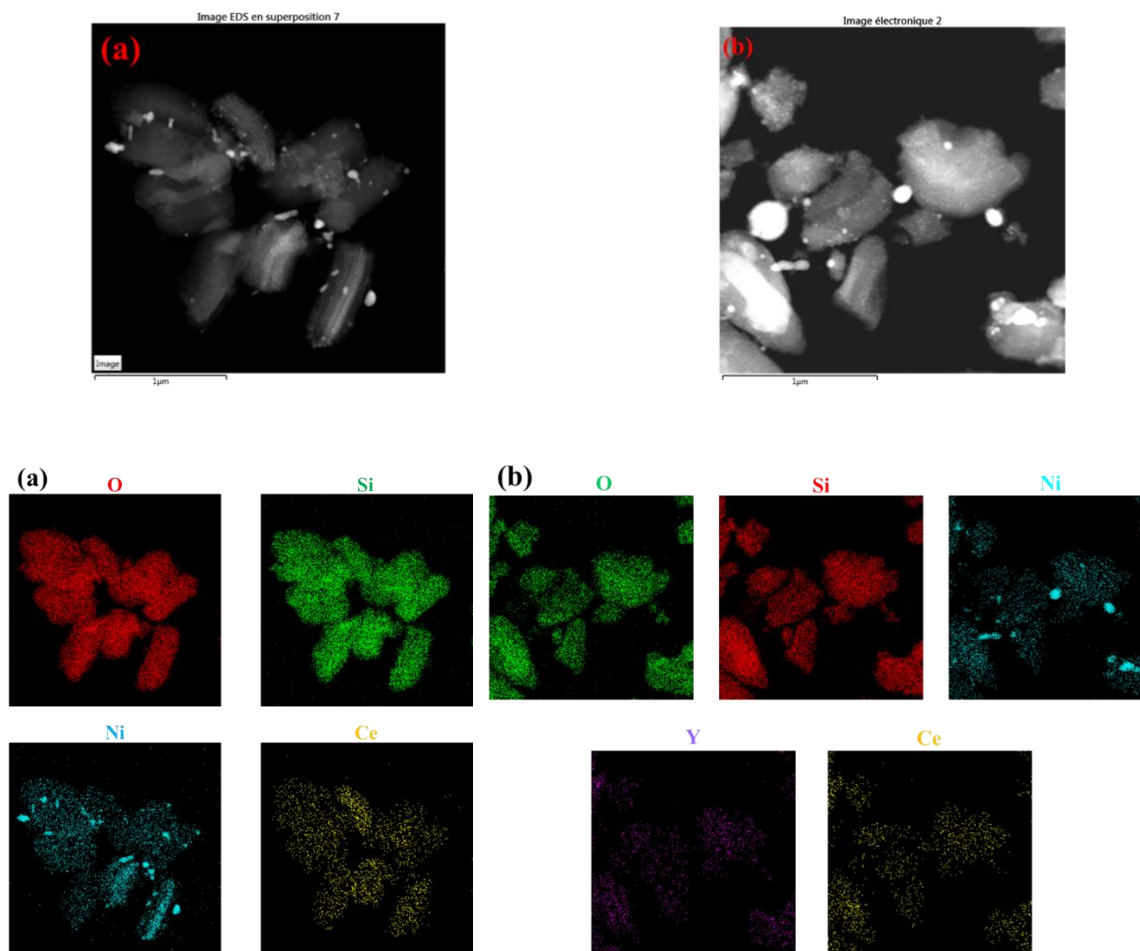


Figure. 6.7. EDS elemental mapping analysis performed for the reduced catalysts: (a) 15Ni10Ce/SBA-15, (b) 15Ni10Ce10Y/SBA-15

EDS elemental mapping analysis was carried out for 15Ni10Ce/SBA-15 and 15Ni10Ce10Y/SBA-15 and presented in Fig. 6.7a and b. In the former, cerium species were well dispersed over the support, whereas nickel was exposed in the form of big particles, as well as uniformly distributed nanoparticles. 15Ni10Ce10Y/SBA-15 revealed Y and Ce species evenly dispersed and less agglomerated particles of Ni. The reducibility of the studied catalysts will be described in detail in the next section.

To investigate the surface composition and oxidation states of the catalysts, the XPS characterization was performed for the reduced catalysts. The XPS spectra are shown in Fig. 6.8 and the atomic ratio and binding energies were calculated in Table 6.3.

As shown in Fig. 6.8a, the O1s spectrum can be deconvoluted into 3 peaks located at 530.6, 532.5, and 533.4 eV, which were attributed to the metal oxide (O_{OM}), oxygen of silica (O_{OSi}), and surface oxygen species adsorbed on oxygen defects (O_{OH}), respectively [410,411]. As shown in Table 6.3, the increase of Y loading resulted in the increase of O_{OH} species. Thus, it can be seen that the increment of Y loading leads to the increase of oxygen defects [373,375].

As shown in Fig. 6.8b, the overlapped spectra can be deconvoluted into 3 peaks. The intensive peak located at 154.0 eV was assigned to the presence of Si2s. The two weak peaks positioned at 157.5 and 159.8 eV were attributed to the presence of Y3d_{5/2} and Y3d_{3/2} [412]. As the increase of Y loading, the peak intensity of Y₂O₃ increases, indicating more yttria species deposited on the surface of the support. Also, no apparent peak shifts regarding Y3d_{5/2} were registered (Table 6.3). From Fig. 6.8c, it can be seen that the intensity of the Si2p peak, which locates at 103.1 eV, decreases with the increase of Y loading, which can be attributed to the coverage of Ni, Ce, and Y on the surface of the SBA-15 material.

In Fig. 6.8d, the XPS spectra of Ni2p_{3/2} for the for 15Ni10Ce/SBA-15 catalyst consisted of two peaks located at 852.8 and 855.5 eV, which were attributed to the Ni⁰ and Ni²⁺ species, with a shake-up satellite peak at 860.7 eV [413]. As presented in Table 6.3, the Ni2p_{3/2} peak shifted towards higher binding energy as the increase of Y promotion, indicating the Ni species could also be incorporated into ceria lattice [373]. It can be observed in Table 6.3 that promotion of the catalyst with Y lead to a change in the Ni⁰/Ni²⁺ ratio. The addition of 2 wt.% Y resulted in the increase of surface Ni⁰ concentration. However, the Y loading higher than 2 wt.% led to the

decrease of the surface ratio of Ni⁰ species. Based on the XRD results, the Ni particle size over the SBA-15 support did not increase significantly with Y addition. However, the peak of Y₂O₃ may appear when the Y loading reached 10 wt.%. Thus, the decrease of Ni⁰ concentration may be caused by the excess Y species on the surface of SBA-15. Also, the adsorption of oxygen species on the surface of Ni⁰ species cannot be excluded. The surface ratio of Ni as shown in Table 6.3 maintains stable with the increase of Y loading until 4 wt.% and then increases when Y loading reached 10 wt.%, indicating the increased Ni species concentration on the surface of the support for 10 wt.% Y loading promoted sample.

The Ce3d XPS spectra of the catalysts were presented in Fig. 6.8e. With the increase of Y adding, the peak intensity of the Y-doped catalysts did not change largely as comparison with the peak intensity of Y-free catalysts. The Ce3d peak could be deconvoluted to 10 peaks labeled as uⁱⁱⁱ, uⁱⁱ, uⁱ, u, u⁰, vⁱⁱⁱ, vⁱⁱ, vⁱ, v, and v⁰. The components labeled as u⁰, uⁱ, v⁰, and vⁱ were attributed to Ce³⁺ species, and the other components labeled as uⁱⁱⁱ, uⁱⁱ, u, vⁱⁱⁱ, vⁱⁱ, and v were assigned to the presence of Ce⁴⁺ species [141]. From Table 6.3, it can be seen that the ratio of Ce³⁺/Ce over the Y-doped catalysts increased gradually as the increase of Y loading, with the highest ratio of Ce³⁺/Ce obtained over 10 wt.% Y promoted catalyst. Thus, it can be concluded that the dopant of Y promotes the formation of Ce³⁺, and thus more oxygen vacancies are created [361]. The Ce3d peak position in eV for Y-doped catalysts also shows a slight shift as the increase of Y loading towards lower binding energy as the increase of Y loading, which demonstrates the incorporation of Y and Ni inside the Ce lattice over the catalysts. This is consistent with the results from XRD.

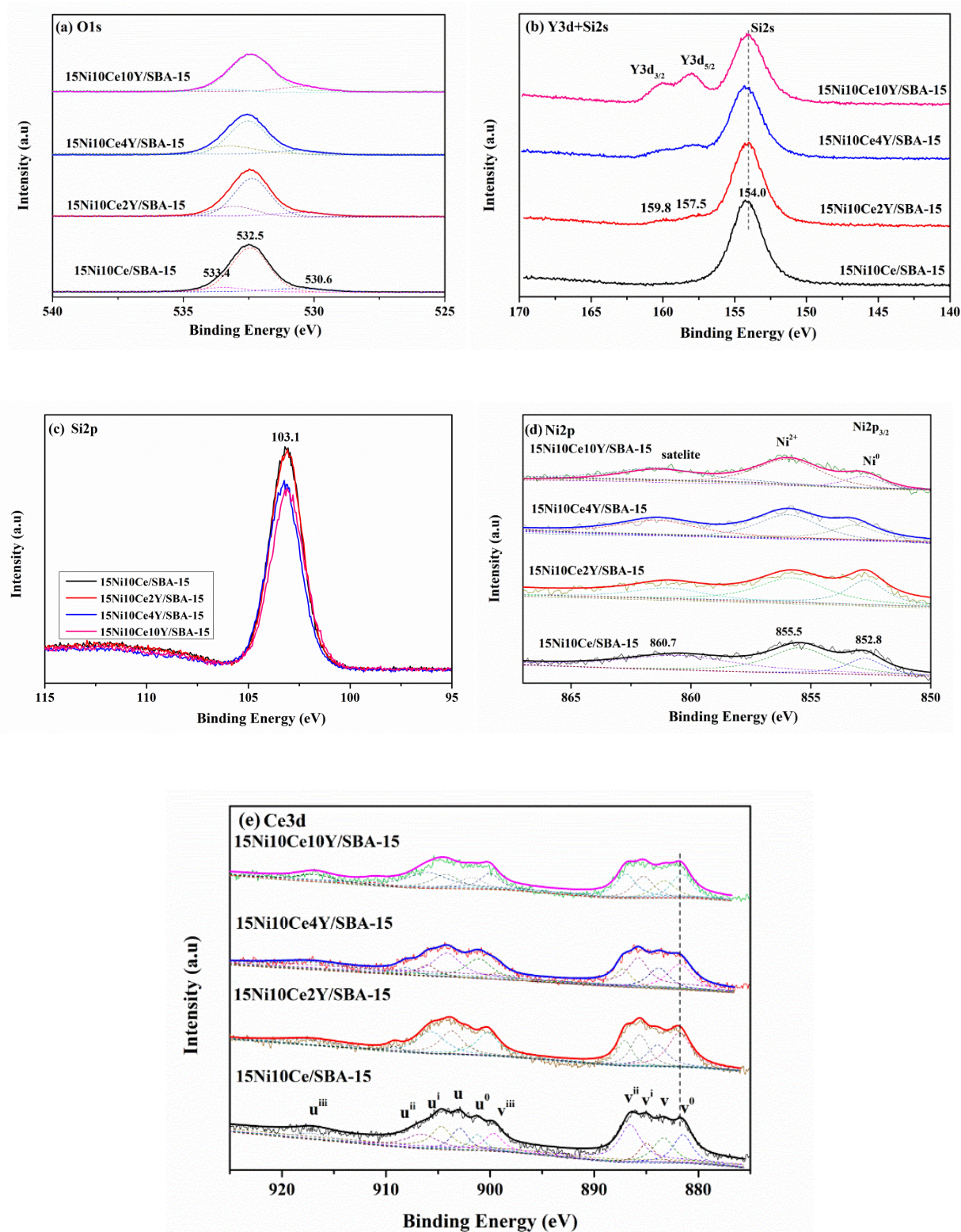


Figure. 6.8. XPS spectra for the reduced samples; Condition: 550 °C reduced under 5% (v/v) of H₂/Ar flow for 1.5h.
(a) O1s, (b) Y3d, (c) Si2p, (d) Ni2p, (e) Ce3d

Table 6.3 XPS derived Ce³⁺ and Ni⁰ percentage, Binding Energy of Y3d_{5/2}, Ni2p_{3/2} and Ce3d_{5/2} in eV, Ni, Ce, and Y atomic ratio for the samples after reduction.

Catalyst	Atomic ratio (%)						Binding Energy (eV)		
	Ni	Ce	Y	Ni ⁰ /Ni ²⁺	O _{OH} /(O _{OM} +O _{OSi} +O _{OH})	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺)	Ni2p _{3/2}	Ce3d _{5/2}	Y3d _{5/2}
15Ni10Ce/SBA-15	1.14	0.56	-	21.8	9.0	48.2	855.5	881.8	
15Ni10Ce2Y/SBA-15	1.00	0.64	3.95	25.9	22.4	50.1	855.8	881.8	157.9
15Ni10Ce4Y/SBA-15	1.04	0.55	4.10	19.1	23.0	51.5	856.0	881.7	157.9
15Ni10Ce10Y/SBA-15	1.20	0.52	4.80	11.7	23.9	57.2	856.0	881.6	158.0

6.2.4 Reducibility of the studied catalysts

The reduction behavior was studied by the H₂-TPR method and presented in Fig.6.9. Four peaks were revealed and labeled as α , β , γ , and δ for Ni15Ce10/SBA-15 and Ni15Ce10Y_x/SBA-15 catalysts (Fig.6.9a-b), and attributed to the reduction of Ni species with different degree of metal-support interactions [414,415]. The peaks centered at the temperature lower than 400 °C (α and β) were attributed to the reduction of NiO species located at the external surface of SBA-15 [415,416]. The peaks centered at 400-500 °C (γ) and 600 °C (δ) were assigned to the reduction of NiO weakly and strongly interacting with the support, respectively [417]. Fig.6.9 revealed a shift of the reduction peaks towards lower temperature with the increment of the Y content, except for the sample with 2 wt.% of Y. This indicates that the reducibility of Y-promoted catalysts has been improved with the increasing loading of yttrium. Table 6.4 presents the H₂ consumption calculated for Y-promoted NiCe/SBA-15 catalysts. The maximum of reduction peaks was lower except for

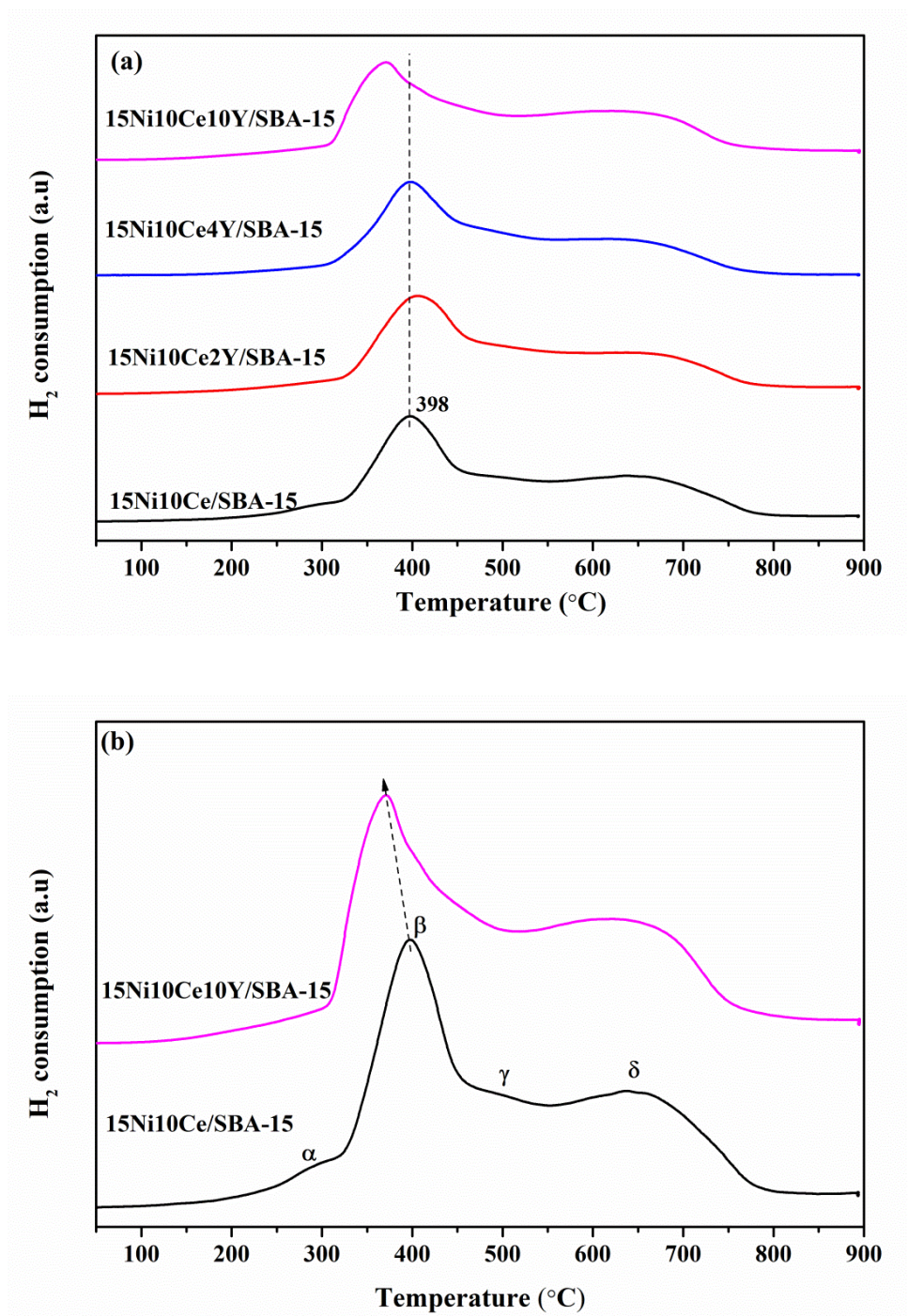


Figure. 6.9. H₂-TPR profiles of the as calcined catalysts (a) and the enlarged mapping of the profiles of 15Ni10Ce/SBA-15 and 15Ni10Ce10Y/SBA-15 (b)

those with 2 wt.% of Y-containing sample. The latter revealed maximum reduction peaks very similar to the 15Ni10Ce/SBA-15 catalyst. TEM micrographs showed an agglomeration of Ni particles in the reduced Ni15Ce10/SBA-15 sample, whereas the presence of Y facilitated the formation of small nickel particles. In this regard, the reducibility of Ni15Ce10Y_x/SBA-15 catalysts has been enhanced.

Table 6.4. The reduction temperature peaks and the H₂ consumption values of the studied catalysts during H₂-TPR

Catalyst	Temperature (°C)				H ₂ consumption (mmol·g ⁻¹)				
	α	β	γ	δ	α	β	γ	δ	Total
15Ni10Ce/SBA-15	299	397	483	665	0.15	0.70	1.30	0.65	2.80
15Ni10Ce2Y/SBA-15	269	401	504	673	0.09	0.84	1.27	0.49	2.70
15Ni10Ce4Y/SBA-15	223	394	455	649	0.02	0.52	1.38	0.63	2.54
15Ni10Ce10Y/SBA-15	238	363	429	622	0.08	0.56	1.07	1.18	2.89

6.2.5 Basicity of the studied catalysts

An adequate number of basic sites is known to play a crucial role in the catalytic performance of CO₂ methanation catalysts. Thus, the basicity of the studied catalysts was investigated by temperature-programmed desorption using CO₂ as a probe molecule. CO₂ desorption profiles are shown in Fig.6.10 and the basic site distribution is listed in Table 6.5. The CO₂ desorption peaks can be classified into three types based on their temperature regions: <220 °C, 220-500 °C, and >500 °C correspondings to weak, medium, and strong basic sites, respectively [141,169,391]. As shown in Table 6.5, the medium basic sites and total basic sites increased with increasing Y

loading with the expense of strong basic sites. The highest amount of medium basic sites was obtained for 15Ni10Ce10Y/SBA-15 catalyst. Pan et al. [160] investigated the reaction route of CO₂ methanation over Ni/Ce_{0.5}Zr_{0.5}O₂ catalyst. The authors suggested that medium basic sites can promote the formation of monodentate carbonates, enhancing activity in CO₂ methanation. Similar observations regarding the beneficial influence of medium basic sites were described elsewhere [141,179,391]. In the current study, the enhancement of moderate basicity can be attributed to the increase of the Ce³⁺ ratio shown in XPS. The incorporation of Y resulted in an increase of the Ce³⁺ ratio, thus more CO₂ species were adsorbed on the generated oxygen vacancies [141].

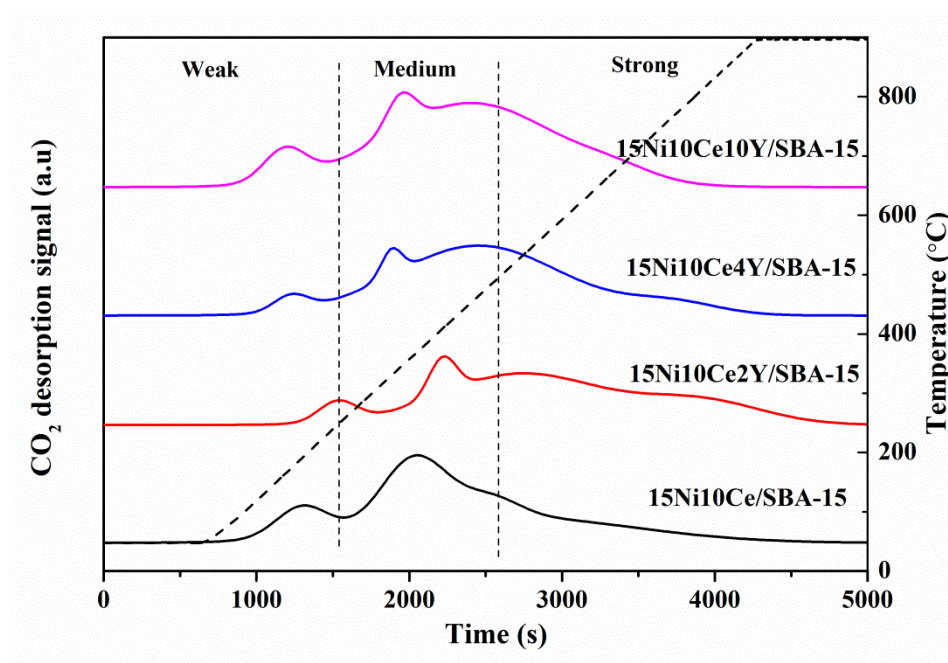


Figure. 6.10. CO₂ desorption curves of the catalysts after reduction at 550 °C for 1.5h.

Table 6.5. The basic site distribution calculated from CO₂-TPD for the reduced catalysts.

Catalyst	Basic sites [\square mol/g _{cat}]			Total basic sites	Distribution of basic sites [%]		
	weak	medium	strong		weak	medium	strong
15Ni10Ce/SBA-15	6.7	23.0	24.6	54.3	12.4	42.3	45.3
15Ni102YCe/SBA-15	3.2	38.5	11.8	53.5	6.0	72.0	22.0
15Ni10Ce4Y/SBA-15	2.2	50.5	4.6	57.4	3.9	88.1	8.0
15Ni10Ce10Y/SBA-15	5.4	64.4	2.6	72.5	7.5	88.9	3.6

6.2.6 Catalytic performance in CO₂ methanation

The catalytic activity and CH₄ selectivity of NiCe/SBA-15 catalysts promoted with Y are presented in Fig.6.11a and Fig.6.11b. The blue dash lines in both figures represent the thermodynamic equilibrium of CO₂ conversion and CH₄ selectivity in CO₂ methanation for the assumed experimental conditions. CO₂ conversion, obtained for the studied catalysts, increased with the increasing reaction temperature and reached nearly equilibrium at 450 °C. In the temperature range of 300-350 °C, in which the conversion values of the catalysts are distinguished, it can be seen that yttrium promoted catalysts showed higher CO₂ conversion compared to that of Ni15Ce10/SBA-15. Depending on the loading of yttrium, the following activity order was observed at 350°C: 10Ce (40.0%) < 2Y (44.0%) < 4Y (54.5%) < 10Y (61.2%), in which 10Ce refers to the 15Ni10Ce/SBA-15 sample.

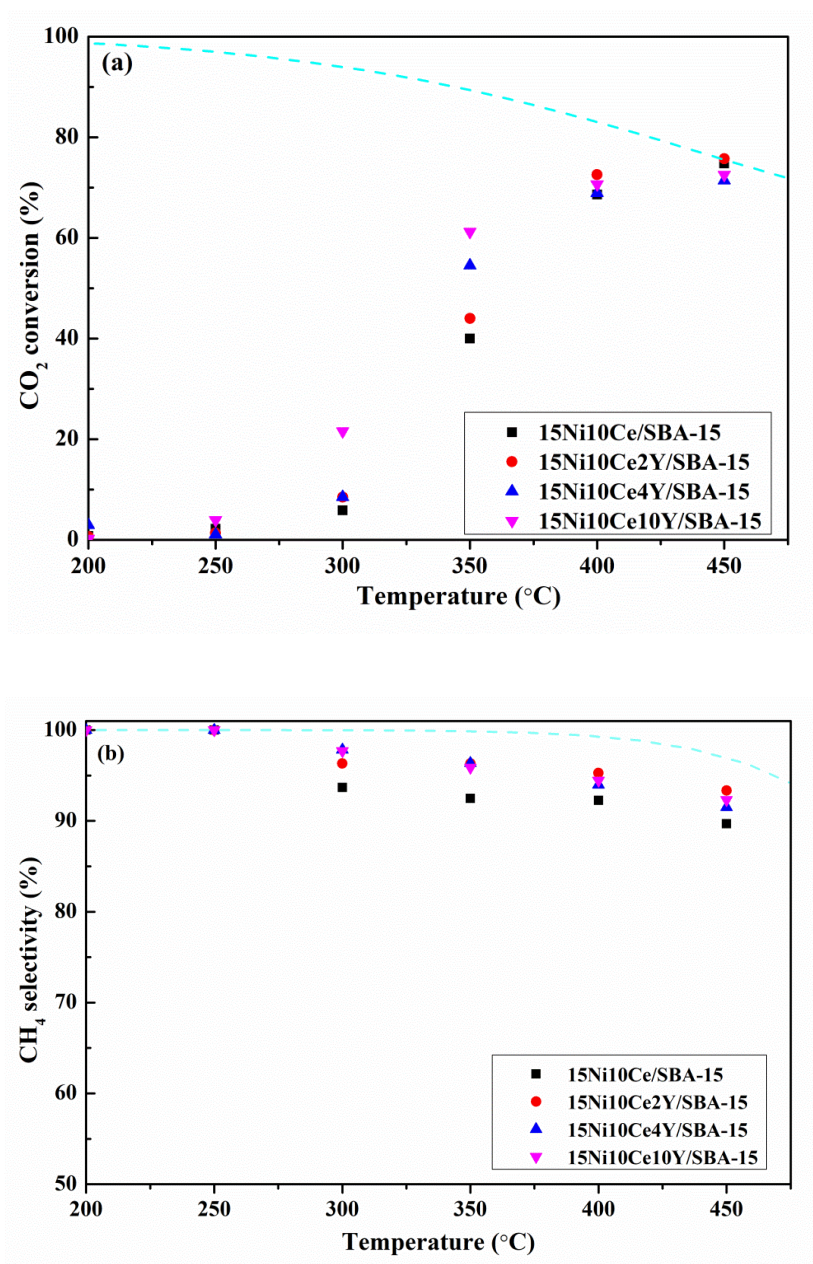
Fig.6.11b shows selectivity to CH₄, revealing a gradual decrease with the temperature rise. At temperatures lower than 300 °C, there is no difference in the CH₄ selectivity for all catalysts as the CO₂ conversion is negligible in this temperature region. In the temperature window between 300 and 400 °C, the Y-free catalyst showed the lowest CH₄ selectivity. Meanwhile, the series of Y-

promoted catalysts showed equally high CH₄ selectivity. It is worth noting that only carbon monoxide (CO) was registered as a side product in the studied reaction conditions. The formation of CO is mainly caused by the reverse water-gas shift reaction ($\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$) [418]. According to the thermodynamics of the CO₂ methanation reaction, the CO selectivity increases with the increasing temperature, consequently decreasing selectivity towards CH₄ production [418,419]. It has been reported that the Ce promotion of Ni/SBA-15 catalyst can increase the activity and CH₄ selectivity in CO₂ methanation [178,224]. The presence of cerium can enhance the activation of CO₂ at low temperatures, hence improve the activity and CH₄ selectivity [221]. Herein, the promotive effect of Y on NiCeY/SBA-15 catalysts was observed.

The catalytic performance of yttrium individually doped Ni/SBA-15 catalysts were also displayed in Fig.6.11c and d. It can be seen that the Ni/SBA-15 catalysts doped by yttrium show worse activities compared to those catalysts doped by Ce and Y.

It has been reported that the methanation mechanism over Ni-containing SBA-15 and MCM-41 mesoporous silicas undergoes the route of CO-free and without the participation of intermediates, such as carbonate and formate [221]. In the study of Bacariza et al. [221], FTIR analysis carried out for Ni/SBA-15 catalyst showed the adsorbed CO₂ species on the surface of Ni metal transformed to carbonate species, following the formation of formate species, then led to the formation of methane. However, many carbonyl species could be formed over the catalysts, which accounted for the formation of CO and the feasible poisoning of metallic nickel. In the CO₂ adsorption experiment carried out with the assistance of FTIR, only CO species (probably originating from the CO₂ disproportionation/dissociation reaction) were found over the bare SBA-15 support, which suggests that the methanation reaction could not occur in the presence of Ni metal [221]. When Ce was loaded onto the Ni/SBA-15 catalyst, the carbonyl species that led to

the formation of CO decreased, consequently promoted the activation of CO₂ and enhanced the formation of CH₄. The promotion effect of Ce for Ni/SBA-15 catalyst in CO₂ methanation was undisputed [178]. Moreover, the promoting effect of Y on Ni/CeO₂ catalysts has been reported in CO₂ methanation, in which the addition of Y can lead to an increase of weak and medium basicity, more oxygen vacancies, and enhanced metal-support interaction [141].



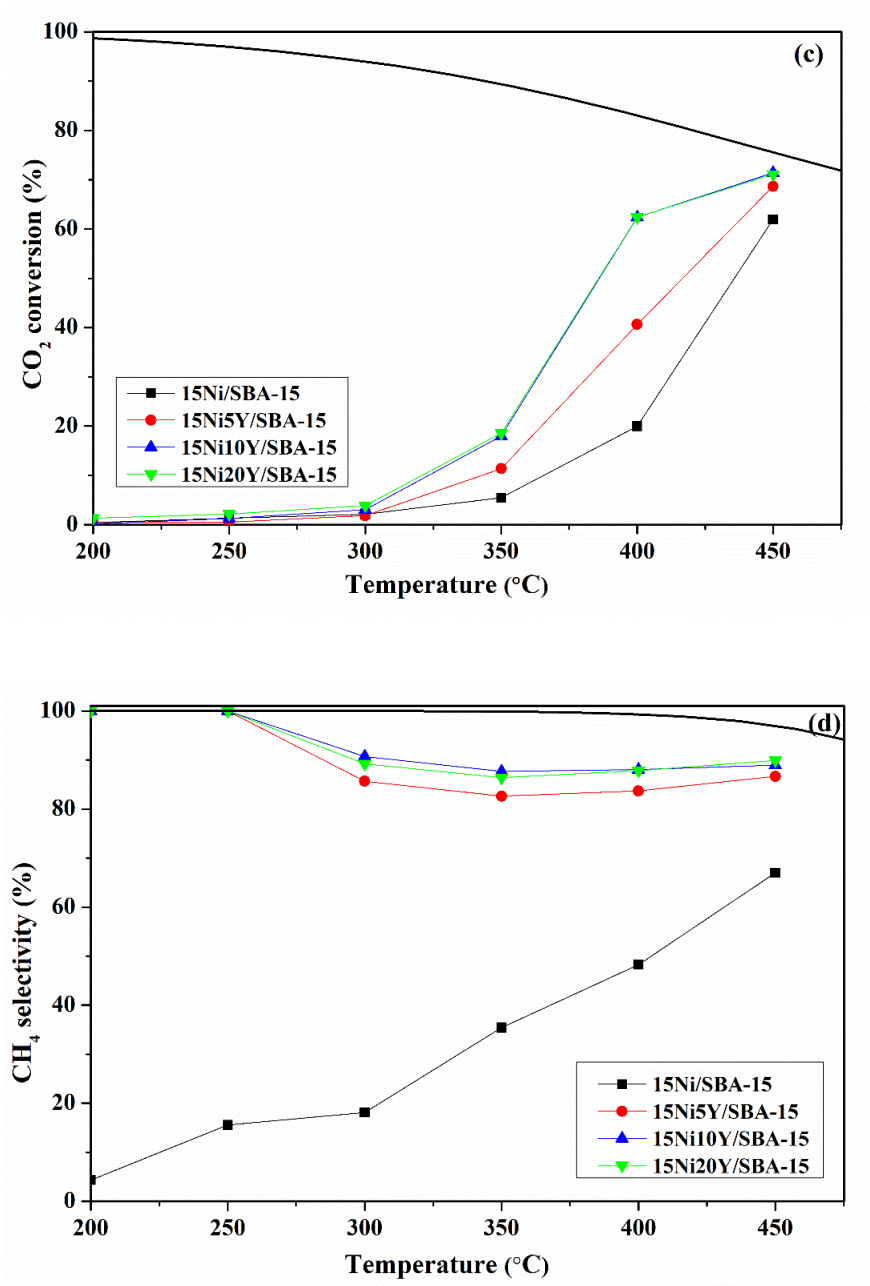


Figure. 6.11. The CO₂ conversion (a) and CH₄ selectivity (b) of NiCe/SBA-15 catalysts with and without yttrium in CO₂ methanation; CO₂ conversion (c) and CH₄ selectivity (d) of yttrium promoted Ni/SBA-15 catalysts.

In the current study, the presence of Y promoted the reduction of Ni species of 15Ni10Ce_xY/SBA-15 catalysts, as proven by the H₂-TPR experiment. Meanwhile, the formation of solid solution of Y-Ce was demonstrated by XPS. Also, the addition of Y could lead to the increased ratio of

$\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$, with 10 wt.% Y-modified catalysts having the highest ratio of $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$, and favoring an increase of oxygen vacancies. The latter is believed to promote the activation of CO₂ [141]. Moreover, CO₂-TPD results show that the presence of yttrium oxide can contribute to the increase of medium-strength basic sites, which are advantageous in CO₂ methanation [160]. In our study, the 10 wt.% Y-modified catalysts presented the highest number of medium basic sites, which can explain the increased CO₂ conversion and CH₄ selectivity.

By correlating the CO₂ conversion at 350 °C with the ratio of $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ (Fig.6.12a), a linear correlation can be found between $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ ratio and the increasing Y loading. With increasing Y loading up to 10 wt.%, the ratio of $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ and CO₂ conversion increase linearly. Furthermore, CO₂ conversion at 350 °C can be also correlated with the amount of medium basic sites as shown in Fig.6.12b. With the increasing Y content, both CO₂ conversion and number of medium basic sites increased until 10 wt.% of Y. Promotion of 15Ni10Ce/SBA-15 catalysts with the appropriate loading of yttrium can improve the Ni dispersion and its reducibility, increase the ratio of $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$, and enhance the moderate basicity. All these factors can positively influence CO₂ conversion and CH₄ selectivity in CO₂ methanation reaction.

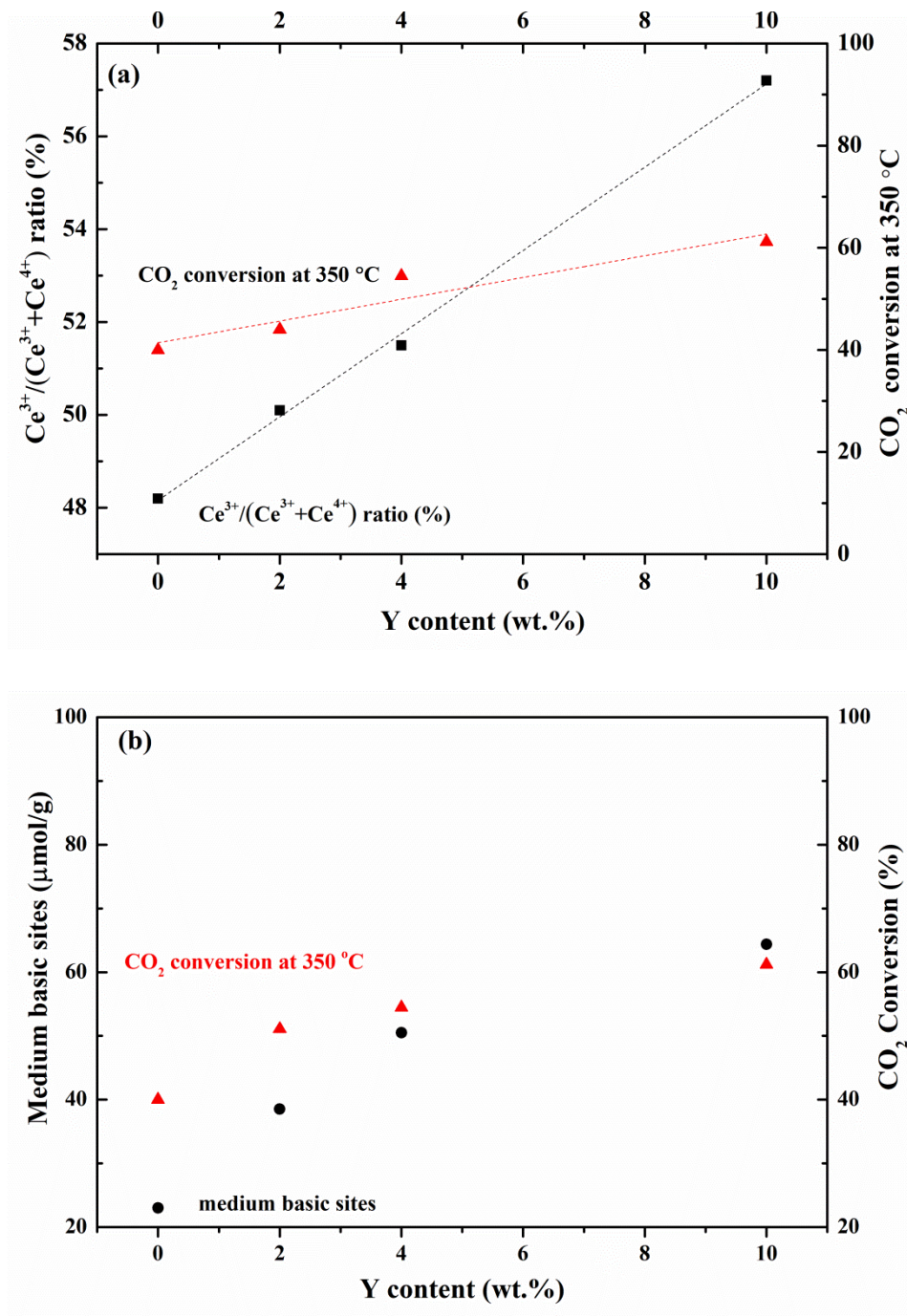


Figure. 6.12. Correlation between the CO₂ conversion at 350 °C with the ratio of Ce³⁺/(Ce³⁺+ Ce⁴⁺) (a) and medium basic sites (b) with the 0 wt.% Y representing the NiCe/SBA-15 sample.

6.2.7 Stability tests of NiCe/SBA-15 and NiCeY/SBA-15 catalysts at 350 °C

The stability tests were performed at 350°C for 15Ni10Ce/SBA-15, 15Ni10Ce4Y/SBA-15, and 15Ni10Ce10Y/SBA-15 catalysts. Fig. 6.13a shows stable CO₂ conversion values during 7 h of time-on-stream (TOS) experiments. The highest CO₂ conversion was measured for 15Ni10Ce10Y/SBA-15, in good agreement with previously conducted experiments (Fig. 6.11a). In Fig. 6.13b, the catalysts modified with 4 and 10 wt.% of Y showed nearly the same CH₄ selectivity values during the stability test. Nevertheless, the 15Ni10Ce/SBA-15 catalyst showed a slight loss in CH₄ selectivity after the 2 h test, which may be caused by the formation of Ni carbonyls, leading to the possible sintering of Ni metal and formation of CO species [221]. Carbon monoxide is a side product of parallelly occurring reactions during CO₂ hydrogenation, i.e. reverse-water gas shift [420]. On the other hand, carbon monoxide production can be associated with a deactivation of metallic nickel nanoparticles. Zurrer et al. [421] studied differently modified NiMg-MOF-74 mixed metals catalysts in CO₂ methanation. The authors reported that the selectivity tends toward CO production rather than CH₄ for the catalysts containing the most content of nickel (80Ni20Mg and 100Ni). Once the nickel particles are encapsulated by graphitic carbon, a reduction of the adsorbed CO intermediate is diminished due to a hydrogen deficient environment. Another explanation can be a change in the nickel-metal electronic state caused by the carbon shell formation. In the latter case, the resulting product can be carbon monoxide. Both hypotheses imply the importance of the usage of a carbon-resistant catalyst in CO₂ methanation.

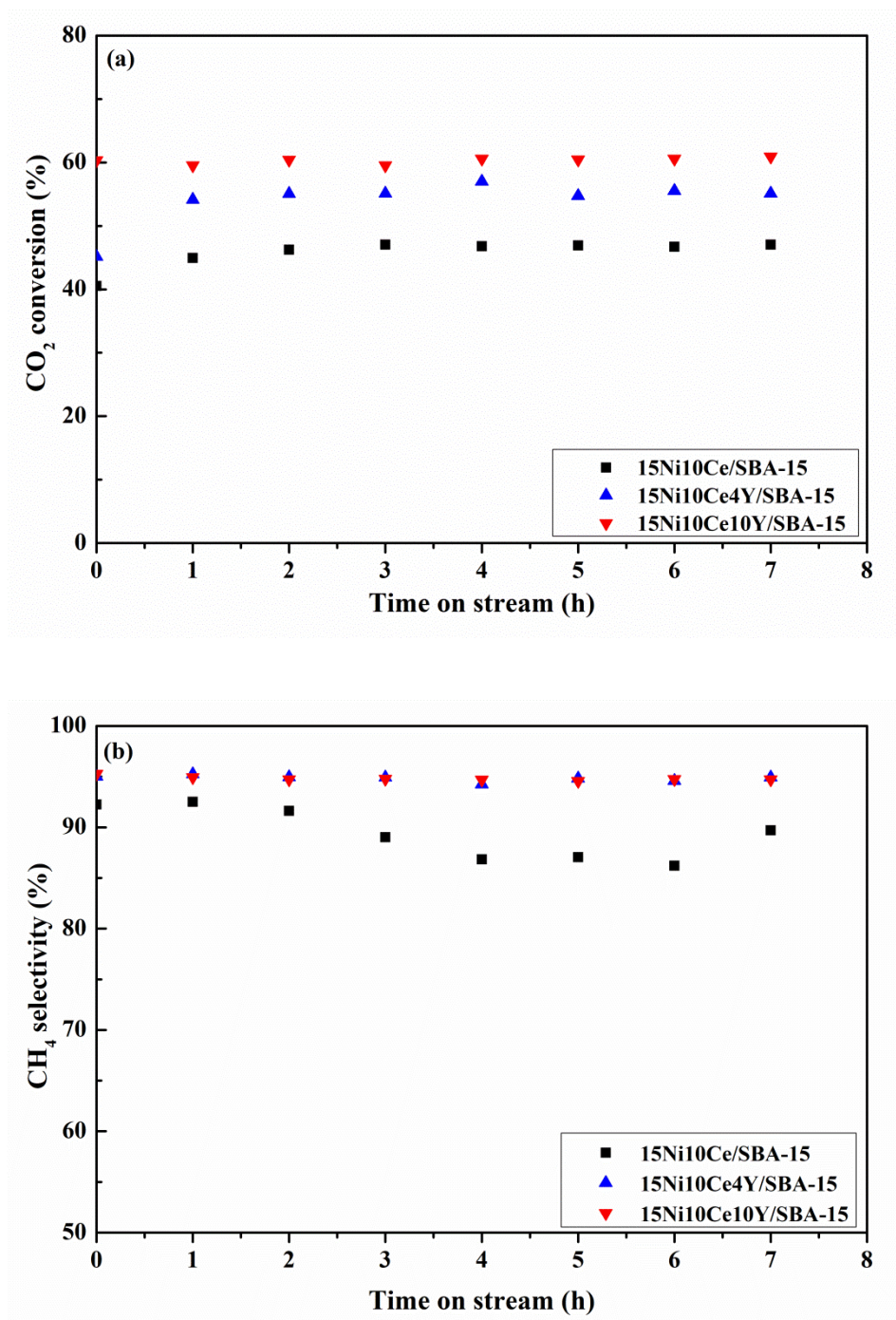


Figure. 6.13. The stability tests of CO₂ methanation over selected NiCe/SBA-15 and NiCeY/SBA-15 catalysts; (a) CO₂ conversion versus time; (b) CH₄ selectivity versus time. Experimental conditions: 350 °C, H₂/CO₂/Ar=60/15/25, GHSV=12,000h⁻¹.

6.2.8 Characterization of catalysts after CO₂ methanation reaction

6.2.8.1 XRD patterns of the catalysts after test

Wide-angle XRD measurements were carried out to investigate the structural features of the catalysts after CO₂ methanation. Fig.6.14 presents that nearly no changes of the diffraction peaks were registered, compared to the XRD results recorded for the reduced catalysts (Fig.6.5b). No reflection peak arising from graphitic carbon was observed. These observations can be ascribed to the good confinement of the SBA-15 structure which suppressed the sintering of nickel [179]. Nevertheless, the crystal size of metallic Ni metal was rearranged after the reaction (Table 6.6), which can be attributed to the formation of carbonyl species formed on the surface of Ni metal, leading to a partial deactivation of the catalyst [144,221].

6.2.8.2 TGA-MS tests of catalysts after test

Thermogravimetric analysis was performed to examine the existence of carbon deposits formed during CO₂ methanation. The registered curves are shown in Fig. 6.15. Spent 15Ni10Ce10Y/SBA-15 catalyst was decomposed in air, revealing the formation of products with mass signals of $m/z=18$ (H₂O) and $m/z=44$ (CO₂). The first weight loss registered in the temperature range from 35 to 200°C can be attributed to the removal of water molecules from the SBA-15 supported catalyst. The second mass change occurred between 200 and 400°C and can be related to desorption of the adsorbed molecules during the reaction, e.g. CO₂ ($m/z=44$). The mass gain is a result of Ni⁰ oxidation into NiO crystallites [217]. The third mass change was recorded between ca. 400 and 900°C which can be linked with possible oxidation of deposited carbon, however, that was not the case for our spent catalyst as no change of the $m/z=44$ signal was registered (C+O₂=CO₂).

Moreover, no mass difference was recorded above 800°C, excluding the existence of graphitic carbon.

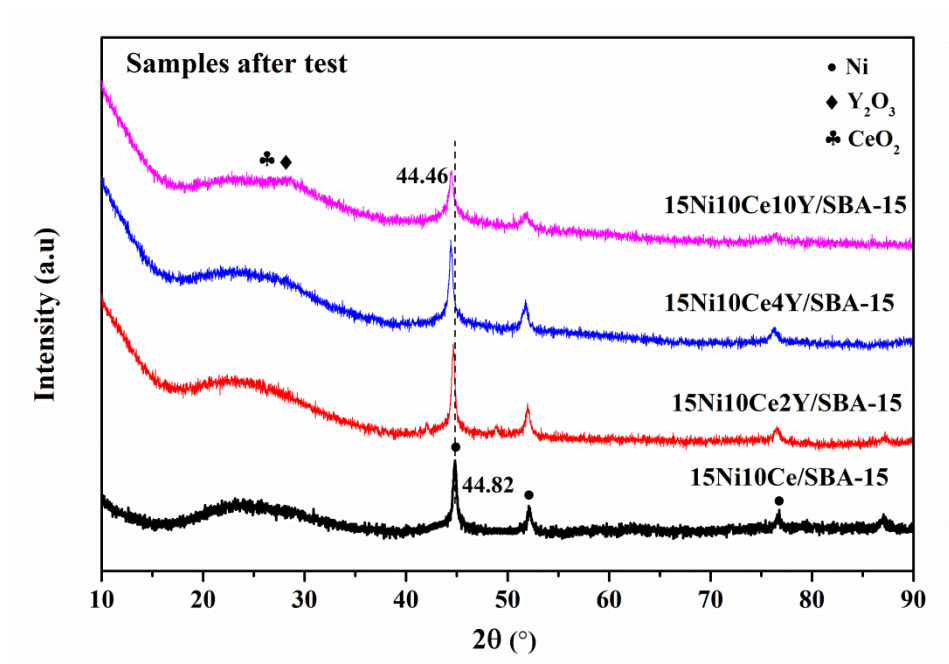


Figure. 6.14. XRD patterns of the catalysts after CO₂ methanation tests.

Table 6.6. Ni metal crystallite size calculated from XRD by Scherrer equation for the catalysts after methanation reaction.

Catalyst	Ni metal crystallite size (nm)
15Ni10Ce/SBA-15	18.8
15Ni10Ce2Y/SBA-15	17.6
15Ni10Ce4Y/SBA-15	16.8
15Ni10Ce10Y/SBA-15	16.4

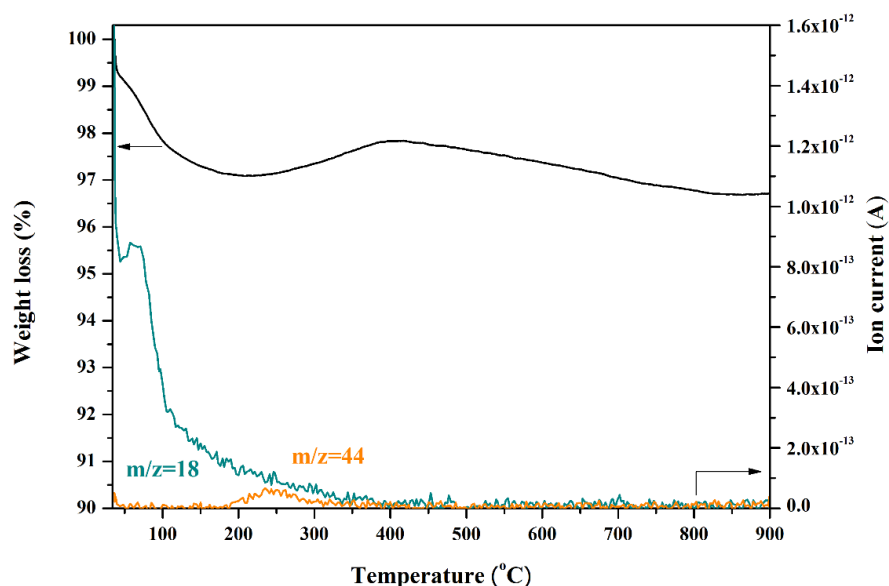


Figure. 6.15. Thermogravimetric analysis coupled with mass spectrometry carried out for 15Ni10Ce10Y/SBA-15 catalyst used in CO₂ methanation for 7 h at 350 °C.

6.2.9 Conclusions of Ce and Y promoted Ni/SBA-15 catalysts

A series of NiCeY/SBA-15 catalysts were characterized and tested in CO₂ methanation. The effect of yttrium promotion on SBA-15-supported Ni-Ce catalysts was investigated in CO₂ methanation. The microscopy analyses revealed that modification with Y positively affects the distribution of Ni particles, being extensively dispersed inside the mesoporous channels of SBA-15 silica support. Moreover, yttrium as a promoter contributed to an increase of $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ ratio and the number of medium basic sites, enhanced the reducibility of nickel species, and led to the formation of a Y-Ce solid solution. NiCeY/SBA-15 catalysts showed better catalytic performance in CO₂ methanation than Y-free catalyst, with the highest CO₂ conversion and CH₄ selectivity measured for 10 wt.% Y loading. Both 15Ni10Ce/SBA-15 and 15Ni10Ce10Y/SBA-15 catalysts revealed

stable CO₂ conversion without an activity loss during 7 h of time-on-stream (TOS) experiment at 350°C. In addition, the modification with yttrium favors selective CO₂ hydrogenation towards CH₄ production. 15Ni10Ce10Y/SBA-15 showed excellent coking resistance and anti-sintering ability, which can be attributed to the confinement of the SBA-15 structure. Meanwhile, although increases of activity and selectivity of Ni/SBA-15 catalysts doped by yttrium were found, they were lower compared with Ce and Ce-Y doped NiCe_xY/SBA-15 catalysts.

In conclusion, both Y and Ce show improved effects on the performance of Ni/SBA-15 catalysts in CO₂ methanation. Ce is more superior than Y in individually promoting the activity of Ni/SBA-15 catalyst. The Y-Ce doped Ni/SBA-15 shows the best activities compared to Ni/SBA-15 doped by one promoter.

6.3 SBA-16 supported Ni catalysts for CO₂ methanation: on the effects of Ce or Y promoter

6.3.1 Ce promoted Ni/SBA-16 catalysts for CO₂ methanation

6.3.1.1 Introduction

Mesoporous silica materials have unique mesoporous structure and textural properties such as a high specific surface area (SSA), a large porous volume, and high thermal stability, which could confine the particle of Ni [389]. The mesoporous silica like SBA-15, KIT-6, MCM-41, and SBA-16 had been widely used as supports in various catalytic reactions [50,389,422,423]. It was found that the mesoporous structure of the support could facilitate the formation of smaller Ni particles and suppress the mobility of Ni particles at high temperatures, thus promote the activity and stability of catalyst [422]. MCM-41, SBA-15, and USY zeolite had been employed as support in the preparation of Ni catalysts for CO₂ methanation and it was found that the Ni species were highly dispersed in the mesoporous framework of the support [171,221,347,423]. However, the two-dimensional mesoporous materials like SBA-15 and KIT-6 still encounter insufficiently suppressing the sintering of Ni particles at high temperature as the movement of Ni particles in the channels or on the external surface, which is caused by the weak interaction between nickel and the support [424]. Thus, three-dimensional mesoporous material e.g., SBA-16 could be an alternative for the stabilization of Ni metal particles.

The SBA-16 supported Ni catalysts have been already used in CO₂ methanation reaction and other CO₂ utilization reaction [182,204,389,425]. It was found that smaller particles were formed within the mesopores of SBA-16 material as the confinement effect of cubic cage-like mesopores and thick pore walls [204]. In addition, the Ce promoter had a remarkable effect on the structural

stability of the Ni particles and SBA-16 framework [389]. Moreover, it has also been reported that Ni catalysts supported on Ce-incorporated-SBA-16 showed a good activity toward the chemical looping steam methane reforming (CL-SMR) process and DRM reaction as the smaller Ni metal particles in the presence of Ce, which prevented the coke formation [389,425]. The undoped Ni/SBA-16 catalysts reported in the literature did not show satisfactory activities in CO₂ methanation. Thus, it is important to try to improve the performance of Ni/SBA-16 catalysts via doping various additives. Considering the advantages of the Ce promoter, it could be a promising additive for Ni/SBA-16 catalysts in CO₂ methanation.

In this chapter, the Ni/SBA-16 catalysts doped with different loading of Ce were synthesized and the effect of Ce loading on the catalytic performance of Ni/SBA-16 catalyst for CO₂ methanation reaction was investigated. XRD, N₂ physisorption, TEM/HRTEM, XPS, H₂-TPR, and CO₂-TPD technologies were used to characterize the physicochemical properties of the supports and catalysts to drive a correlation between the physicochemical properties of the catalysts and their activities in CO₂ methanation.

6.3.1.2 Materials preparation and characterization

The SBA-16 material was synthesized by the hydrothermal method and the detailed process was depicted in 3.1.4.2 of chapter 3.

The Ni/SBA-16 and Ce-promoted Ni/Ce/SBA-16 catalysts with different Ce content were synthesized by the wet impregnation method described in 3.1.4.2 of chapter 3. The catalysts were denoted as 10Ni/xCe/SBA-16 (x represents the weight percent relative to support).

The textural properties i.e. SSA, pore volume (V_p), and average pore size (r_p) of the calcined materials (supports and catalysts) were measured by N₂ adsorption-desorption technology described in chapter 3.

The XRD and TEM/HRTEM experiments followed the process in chapter 3.

The X-ray photoelectron spectra (XPS) were recorded for reduced samples on a Thermo Scientific ESCALAB 250Xi spectrometer (Thermo Fisher Scientific Inc.) (different from the apparatus shown in chapter 3) with an Al anode for Ka (1486.6 eV) radiation. The sample was reduced to 500 °C for 1 h in a 5% H₂/Ar mixture (100 mL/min) and then used for the XPS experiment. The charging effects were corrected by adjusting the binding energy of the C1s peak to 284.6 eV and the data was processed by the Thermo Advantage software attaching to the equipment. The Ce3d peak was split into ten components that considered the spin orbit splitting of Ce3d_{5/2} and Ce3d_{3/2}. Four peaks labeled as v⁰ u⁰, vⁱ, uⁱ were attributed to Ce³⁺ species, and six peaks labeled as v, u, vⁱⁱ, uⁱⁱ, vⁱⁱⁱ, uⁱⁱⁱ were attributed to Ce⁴⁺ species [332,426,427].

The reducibility and basicity of the catalysts were evaluated by H₂-TPR and CO₂- TPD shown in chapter 3. The pre-treatment condition for CO₂- TPD was different from chapter 3 and described as below. Before CO₂ adsorption, the sample (60 mg) was reduced in 5% H₂/Ar flow (50 mL/min) at 500 °C for 1 h. Then, the adsorption and desorption process was carried out following the process in chapter 3.

6.3.1.3 Catalytic activity test and stability test

The catalytic activity of catalysts was evaluated by the same process shown in chapter 3. The reduction condition was from ambient temperature to 500 °C and then kept for 1 h with a ramp of

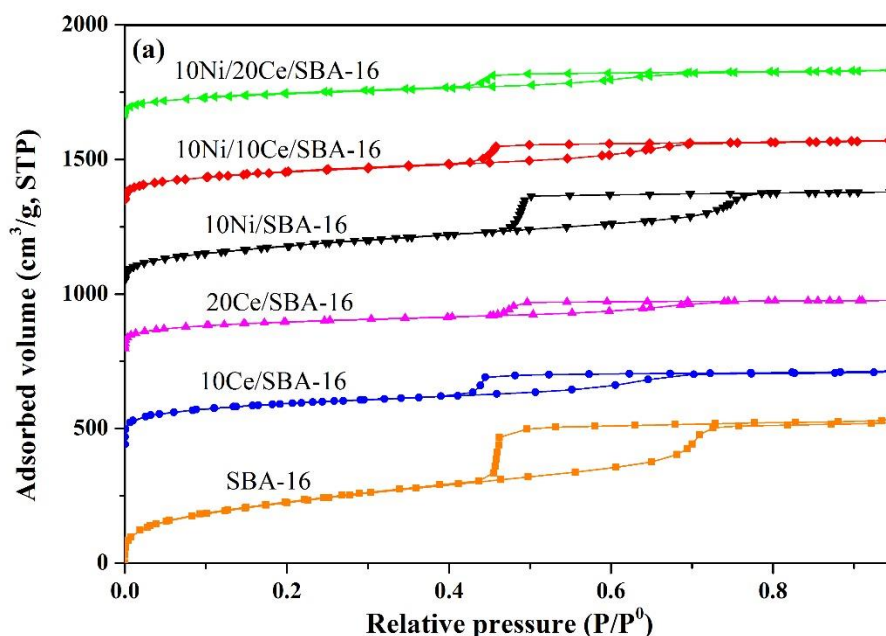
10 °C/min. The reduction temperature was deployed based on the methanation results under different pre-treatment temperatures in which 500 °C showed the best performance

The stability test was performed in the same apparatus as the activity test. The sample (0.5 mL) was reduced at 500 °C for 1 h following cooled down to 350 °C for stability test, with the GHSV of 12,000 h⁻¹. Then, it was maintained at 350 °C for 7 h. The CO₂ conversion and CH₄ selectivity were also calculated following the equations of Eq.1 and Eq.2 in chapter 3.

6.3.1.4 Textural properties, structural properties, morphology, and surface states of elements

The N₂ sorption curves and pore distribution curves of the samples obtained from N₂ adsorption-desorption isotherms were displayed in Fig.6.16. The textural properties were displayed in Table 6.7. As shown in Fig.6.16a, all samples have a type-IV N₂ adsorption-desorption curve with a hysteresis loop located at a relative pressure of 0.40-0.75, suggesting that all samples have ink-bottle mesopores [428]. After loading Ce onto the SBA-16 matrix, there is a decreasing trend regarding the hysteresis loop as the increasing Ce loading, indicating that the Ce was incorporated into the mesopores of SBA-16. A further slight decrease of the hysteresis loop is registered when Ni was loaded. The isotherms of pore size distribution, shown in Fig.6.16b, display that the diameter of primary mesopores of the samples is in the range of 2.6-4.0 nm. It can be seen from Table 6.7 that the fresh SBA-16 material had significantly high SSA and porosity (V_p and r_p). After impregnating the Ce onto the SBA-16 matrix, the SSA and porosity of Ce-doped SBA-16 materials decreased apparently with the introduction of Ce. This can be attributed to the deposition and incorporation of Ce into the pores and onto the surface of SBA-16 [389]. Meanwhile, it was reported that the high calcination temperature could result in the decreases of SSA and mesopores

for ordered mesoporous silicas with spherical mesopores, which could partly account for the decrease of SSA and pore volume for the studied samples [389,429]. After nickel introduction into the SBA-16 and x/SBA-16, further decreases of SSA and V_p (Table 6.7) of catalysts compared with supports were observed for all Ni catalysts, suggesting that the incorporation of Ni into the pores resulted in the blockage of pores of the SBA-16 matrix as already mentioned elsewhere [389]. Moreover, the further shrinkage of the SBA-16 framework also partially happened during the calcination procedure of Ni catalyst, which also accounts for the decreased SSA and the V_p [389]. The pore size of catalysts, however, remained similar or slightly increased when compared to supports, which was also observed in different types of mesoporous silica-supported catalysts [64,189]. Also, the porous structures of SBA-16 for the catalysts remained after Ni and Ce introduction as demonstrated in TEM. In Fig.6.16, it was testified that the ordered structure with cubic cage-like pores of SBA-16 was formed for all catalysts.



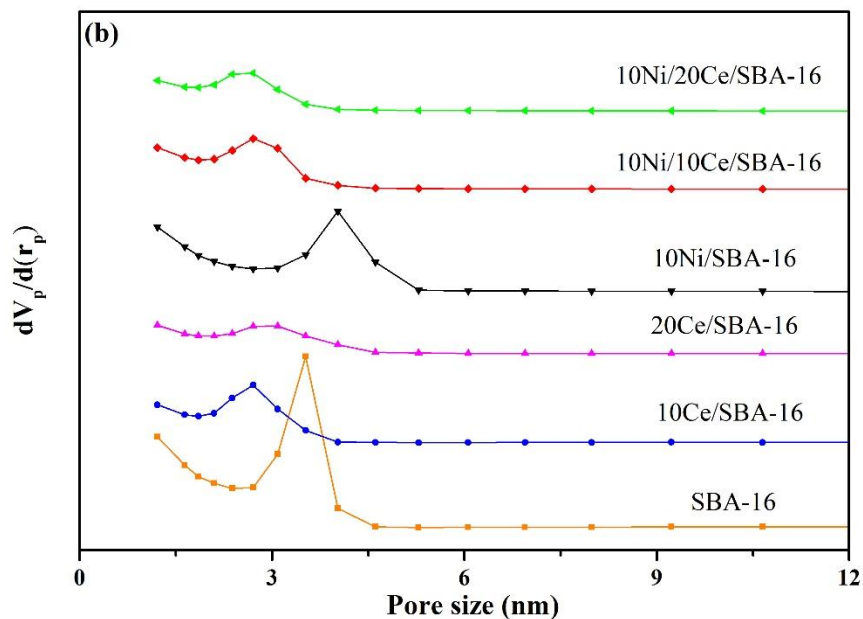


Figure. 6.16. N₂ adsorption-desorption isotherms of samples (a) and pore size distribution of samples (b).

In conclusion, compared to Ni/SBA-16 catalyst, the SSA and V_p of Ce-promoted Ni/SBA-16 catalysts decreased with the increase of Ce loading. The 10Ni/SBA-16 catalyst presented the highest SSA and pore volume, meanwhile, the 10Ni/20Ce/SBA-16 catalyst showed the lowest SSA and V_p .

The SAXRD was performed for the SBA-16 material and displayed in Fig.6.17. As shown in Fig. 6.17, two small peaks at $2\theta=1.25$ and 1.56 were observed for SBA-16 support, representing (200) and (211) reflection, respectively, indicating the existence of ordered mesopores in SBA-16 with body-centered cubic symmetry ($Im3m$) [430].

Table 6.7 BET surface area, pore volume, mean pore diameter from N₂ adsorption-desorption, and the particle size of nickel species calculated from XRD-on calcined samples.

Sample	^a S _{BET} (m ² /g)	^b V _p (cm ³ /g)	^b r _p (nm)	Particle size (nm)	
				^c NiO	^d CeO ₂
SBA-16	934	4.2	3.5	NA	NA
10Ce/SBA-16	536	2.0	2.7	NA	NA
20Ce/SBA-16	402	0.5	1.2	NA	NA
10Ni/SBA-16	630	0.8	4.0	4.3	NA
10Ni/10Ce/SBA-16	484	0.7	2.7	7.7	10.8
10Ni/20Ce/SBA-16	383	0.5	2.7	10.3	10.8

NA: not applicable.

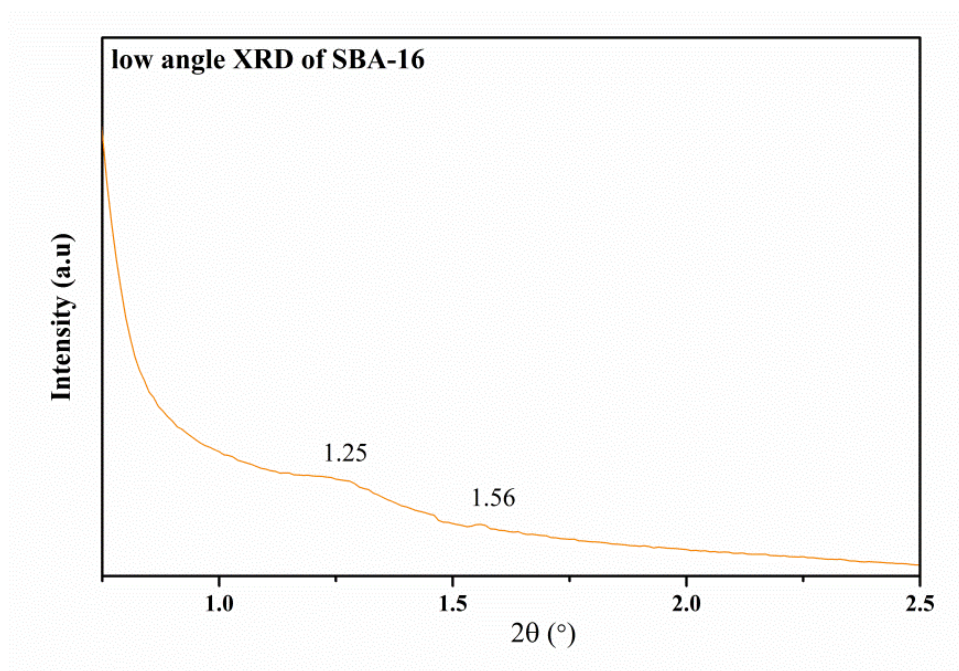
^a The specific surface area was calculated for the calcined sample by the BET method.^b The pore volume and mean pore size was obtained for calcined samples from the BJH method.^c The particle size of NiO was calculated based on the three strong diffraction peaks of the calcined sample by Scherrer Equation.^d The particle size of CeO₂ was calculated based on the four strong diffraction peaks of the calcined sample by Scherrer Equation.

Figure. 6.17. Small-angle XRD (SAXRD) of the synthesized SBA-16 material

The structural properties of calcined and reduced catalysts were characterized by XRD measurements and the patterns were displayed in Fig.6.18. As shown in Fig.6.18a, the XRD patterns showed the existence of an amorphous silica peak at $2\theta=23.2^\circ$ for the SBA-16 support and all the calcined catalysts. Moreover, the intensity of the patterns corresponding to amorphous silica weakens for Ce-promoted catalysts due to the introduction of Ce, which can be caused by the highly dispersed Ce particles on the SBA-16. The diffraction peak of CeO₂ at $2\theta = 28.5^\circ$ affects the diffraction intensity of SiO₂ [415]. A similar effect was also shown over Ce or La-promoted Ni/SBA-15 catalysts [431]. The diffraction peaks of NiO were registered for all the Ni/SBA-16 based catalysts, which are characterized by peaks at $2\theta=37.2, 43.2,$ and 62.8° . They were attributed to the diffraction of the (111), (200), and (220) plane of NiO, respectively [64]. Simultaneously, the diffraction peaks at $2\theta=28.8^\circ, 33.5^\circ, 47.8^\circ, 56.7^\circ,$ and 70.1° were assigned to the diffraction of face-centered CeO₂ cubic lattice [414,432]. The incorporation of Ce into the mesoporous structure of the SBA-16 matrix significantly affected the structure and distribution of Ni species. The diffraction peaks of NiO showed a narrowed trend as the increase of Ce loading in Fig.6.18a. The particle sizes of NiO and CeO₂ nanoparticles were calculated in Table 6.7 using the Scherrer equation. It can be noted that the particle size of NiO increases with the increase of Ce loading. A similar phenomenon was also found by other authors. It had been reported for Ni-Ce/SBA-15 (Ce-promoted Ni/SBA-15, with 6 wt.% Ce and 5 wt.% Ni) catalysts that the particle size of Ni for Ni-Ce/SBA-15 (impregnating Ce first following Ni) could be larger than that of Ni/SBA-15 catalyst but smaller than that of Ce-Ni/SBA-15(impregnating Ni first following Ce) catalyst [432]. Moreover, concerning the diffraction peaks of Ce, there is no significant difference when the Ce loading increases from 10 to 20 wt.%. The particle sizes of Ce were calculated in Table 6.6, with the same particle size (10.8 nm) of Ce for Ce-promoted catalysts. For reduced

catalysts, presented from Fig.6.18b, the broad diffraction peaks of Ni metal and NiO were registered for all catalysts, indicating that the Ni species cannot be reduced completely at 500 °C. There are no significant differences for the diffraction peaks of Ni species after reduction, meaning the Ni species keep stable after reduction. Furthermore, the peak intensity Ce for reduced catalysts remains stable after reduction, indicating the crystallinity and particle size of Ce keep stable.

From XRD measurements, it can be concluded that the Ni species keep highly dispersed over Ni/SBA-16 catalyst. After the incorporation of Ce, the particle size of Ni species increases as the increase of Ce loading for Ni/Ce/SBA-16 catalysts, but the crystallinity and particle size of Ce keep stable. The co-existence of NiO and Ni metal was confirmed over reduced catalysts, with broad peaks of Ni species over catalysts, indicating the Ni species keep dispersed after reduction. And the crystallinity Ce also remains stable after reduction.

In order to obtain the morphology information of the catalysts, TEM and HRTEM analyses were performed over the reduced samples and the images were displayed in Fig.6.19 and Fig.6.20. The TEM micrographs demonstrated that the ordered cage-like mesopores were well-formed in Ni/SBA-16 catalysts with or without Ce (Fig.6.19), although other organization along other directions may be observed depending on the deposition of the samples under the grid [389,433]. In Fig.6.19 (A2, B2, and C2), these images presented a cubic array of uniform channels when the incident electron beam was parallel to the main axis of the mesopores) and also unidirectional or cubic channels when the electron beam took different orientations concerning the sample (Fig.6.19, B2), which demonstrates that the order structure of SBA-16 was preserved despite the incorporation of Ce and Ni into the pores.

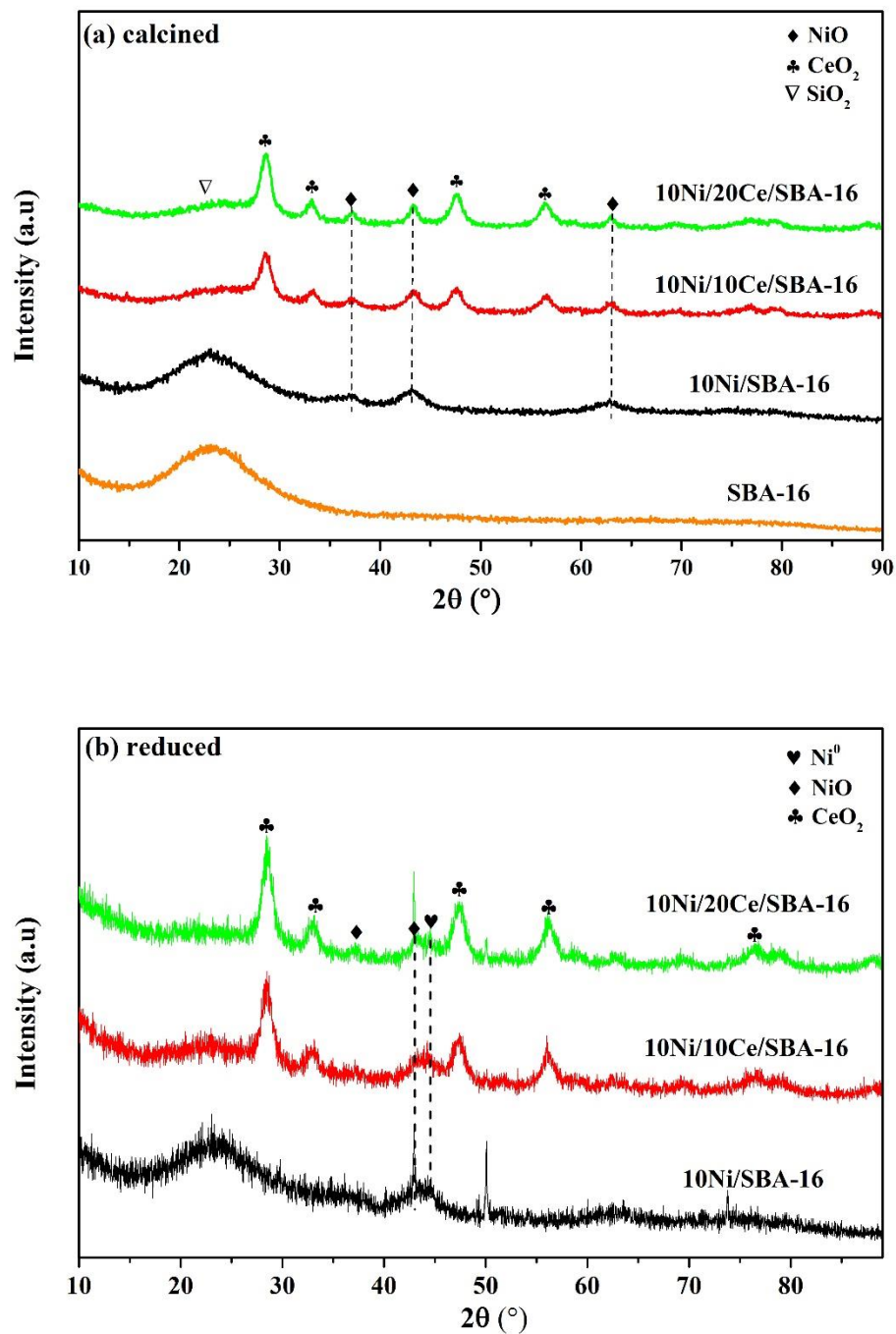


Figure. 6.18. XRD patterns of the Ni/SBA-16 based catalysts by varying Ce loading with SBA-16 as comparison; a) calcined samples at 550 °C in flowing air; b) reduced samples at 500 °C for 1.0 h under H₂/Ar=5/95, flow rate: 100 mL/min

The mesopore size measured by the HRTEM (Fig.6.20b) was about 6.6 nm with a wall thickness of 3.4 nm, which was different from the pore size measured by the BJH method. This can be assigned to the effect of different measurement methods. Fig.6.19B1 and Fig.6.19C1 confirmed also the cubic organization of the porosity of the Ce-promoted Ni/SBA-16 catalyst.

For the 10Ni/SBA-16 sample (Fig.6.19A1), the nickel species were highly dispersed on the SBA-16 matrix, with the measured Ni particle size of 3-5 nm. In Fig.6.20a, dark spots were assigned to the smaller Ni particles observed. On the other hand, the particle size of Ni species for 10 wt.% Ce-doped samples increased when compared to the unpromoted 10Ni/SBA-16 sample, with both NiO (7.7 nm) and Ni particles (6.0-7.5 nm) (Fig.6.20b) identified by the typical reticular distances of 2.4 and 2.03 Å, respectively. The presence of CeO₂ particles was confirmed by the lattice fringes of 3.12 and 1.91 Å corresponding, respectively, to the (111) or (220) planes. They were well dispersed within the support. Their average size is from 5 to 9 nm, which is in line with the result of XRD analyses. Moreover, it should be noticed that by increasing the Ce loading to 20 wt.%, the quality of the dispersion of CeO₂ decreased and aggregates of Ce were observed (Fig.6.19A1). The Ce species were not homogeneous on the SBA-16. Inside the porosity, by HRTEM (Fig.6.20c), larger Ni particles of around 8.2 nm and NiO particles of 9.2 nm, and CeO₂ particles of ca.7-9 nm can also be identified. There are differences regarding the particle size of Ni measured by XRD, which can be assigned to differences of techniques [250]. The XRD measurement only shows the particles with high crystallinity, but the TEM technique can measure the aggregated Ni particles without regard to whether the Ni particles are highly crystalline or not. In both cases, the nickel species were found to be in contact with CeO₂ particles (Fig.6.20b and c). And, it can be concluded that the increase of the Ce loading led to the increase of Ni particles and the aggregates of Ce (20 wt.%).

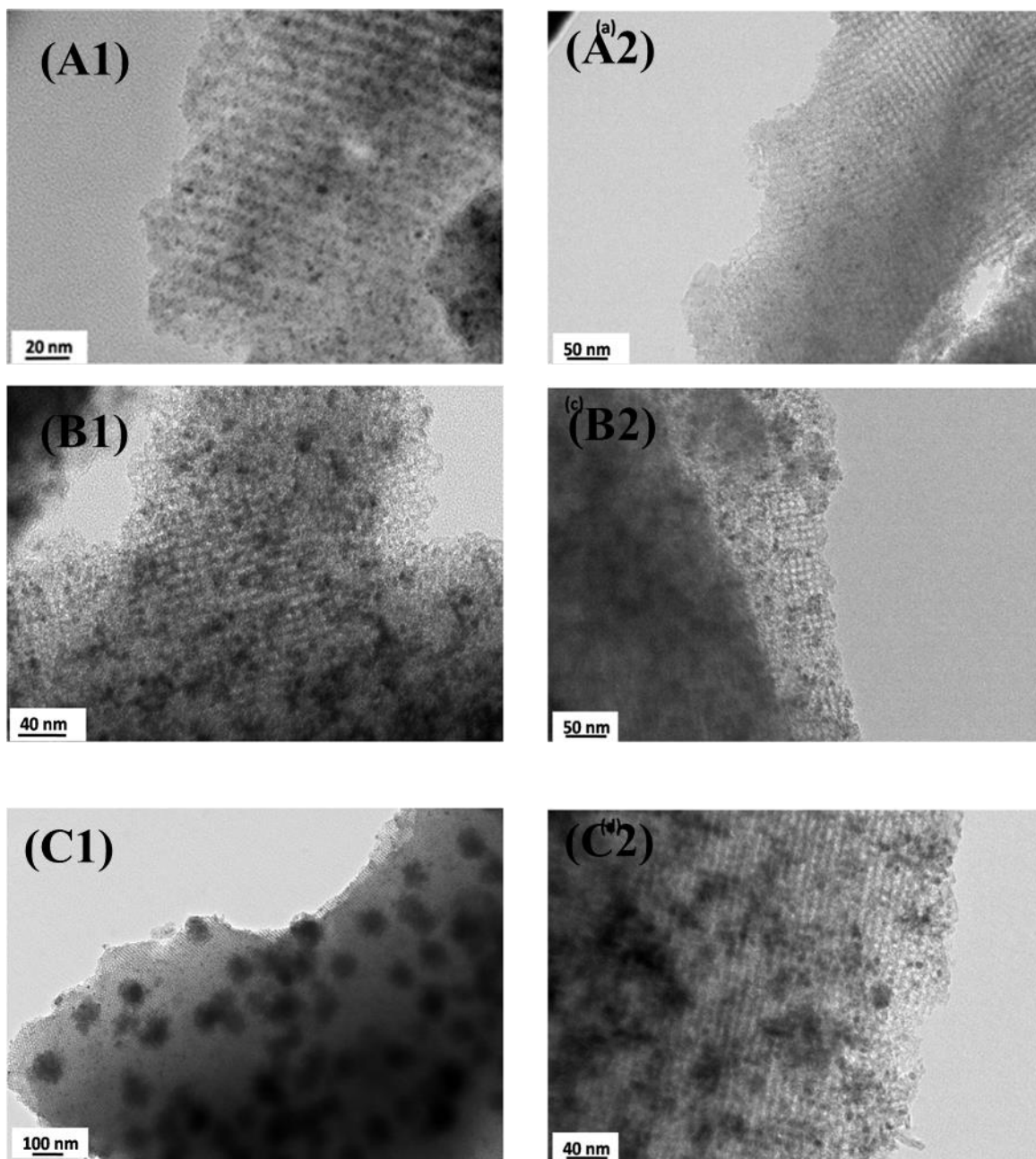


Figure. 6.19. TEM micrographs of the reduced catalysts; Condition: 500 °C for 1 h ($H_2/Ar=5/95$, 100 mL/min); 10Ni/SBA-16 (A), 10Ni/10Ce/SBA-16 (B), 10Ni/20Ce/SBA-16 (C).

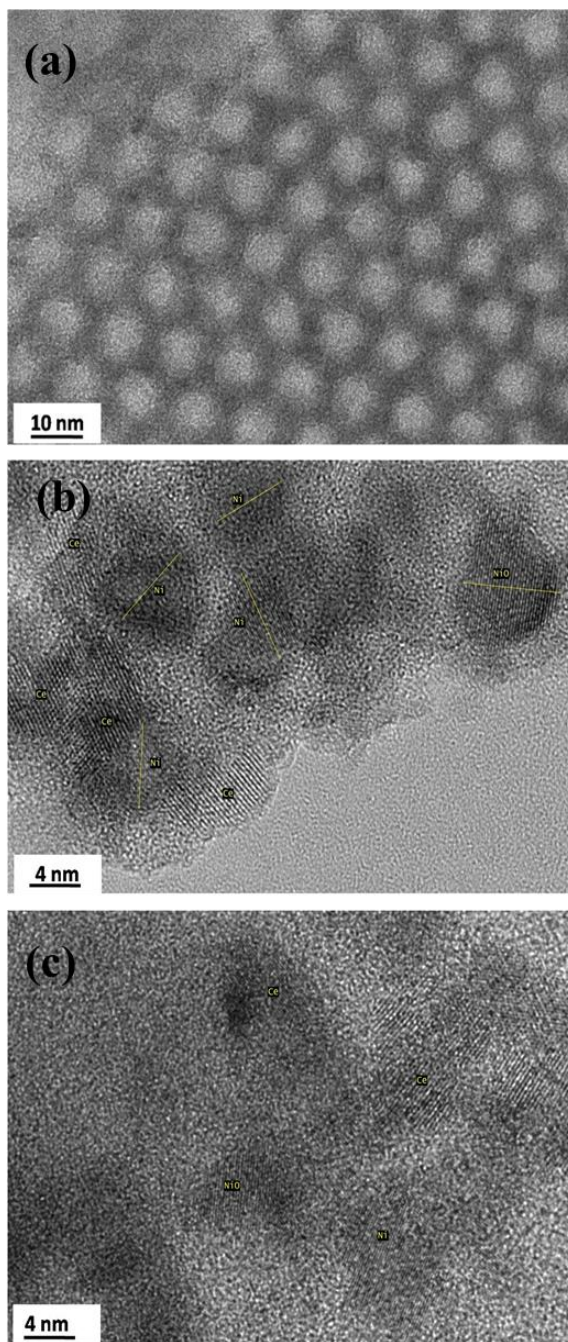


Figure. 6.20. HR-TEM micrographs of the reduced catalysts; Condition: 500 °C for 1 h ($H_2/Ar=5/95$, 100 mL/min); 10Ni/SBA-16 (a), 10Ni/10Ce/SBA-16 (b), 10Ni/20Ce/SBA-16 (c).

In order to study the surface composition and chemical states of Ni and Ce on the reduced catalysts, XPS measurements were carried out over reduced catalysts. The XPS spectra of O1s, Ni2p, Ce3d,

and Si2p have been displayed in Fig. 6.21 and the surface atomic ratios of Ni, O, and Ce species, as well as the binding energies of Ni2p and Ce3d, were presented in Table 6.7. In Fig. 6.21a, it can be seen that the peak located at 533.2 eV, which can be attributed to the superimposed O1s peaks from SiO₂, NiO, and CeO₂ (for Ce-doped samples), corresponding to the lattice oxygen (O_β) [64]. The small peak that appeared at 530.3 eV corresponds to the adsorbed oxygen species (O_α) [64]. As shown in Table 6.8, the percentage of O_α increased with the increase of Ce loading which was agreed with that the presence of ceria promoting the oxygen mobility of catalysts [365]. In Fig. 6.21b, the peak located at 103.9 eV was assigned to the presence of Si2p_{3/2} [64]. The intensity of the Si2p_{3/2} peak decreased with the increase of Ce, which can be attributed to the effect of impregnated Ce on the surface. This is in line with the XRD results. In Fig. 6.21c, the Ni2p_{3/2} binding energy located at 852.8 eV and 856±0.7 eV with a shake-up satellite at 862 eV were attributed to the existence of Ni metal and Ni²⁺ species, respectively [434]. The Ni2p_{3/2} binding energies of Ce-doped samples (Table 6.8) were lower than that of the Ce-free sample, indicating stronger metal-support interaction (MSI) on Ce-doped samples. And the percentage of metallic Ni increases from 4.5% for 10Ni/SBA-16 catalyst to 36.0% for 10Ni/20Ce/SBA-16 catalyst as the incorporation of Ce (Table 6.8), respectively, indicating that the doping of Ce promoted the presence of metallic Ni species on the surface of the catalysts. The XRD results in Fig.6.18b revealed the existence of metallic Ni over 10Ni/SBA-16. However, the XPS result shows nearly complete Ni²⁺ species, which can be attributed to the effect of adsorbed oxygen species on the surface of metallic Ni when exposed to oxygen. The adsorbed oxygen on the surface of Ni metal can promote the formation of a nickel oxide layer [435,436]. The Ni species over 10Ni/SBA-16 catalyst were highly dispersed on the SBA-16 support, resulting in the small nanoparticles of Ni

species (4.3 nm Table 6.7), thus the surface of metallic Ni could be covered by abundant oxygen, forming nickel oxide layers [435,436].

From XPS spectra, The Ce/Si atomic ratio increased with the increase of Ce loading, implying the higher dispersion of Ce species over 10Ni/10Ce/SBA-16 catalyst. The Ni/Si atomic ratio of 10Ni/10Ce/SBA-16 was smaller than that of other catalysts, which could be assigned to the combined effects of small Ni nanoparticles over SBA-16 and coverage of Ni and Ce on the support. As confirmed in BET and XRD measurements, the loading of Ce and Ni resulted in a decrease of SSA, which could give rise to the decrease of Ni/Si ratio on the surface as the covered surface. In TEM, the smaller Ni particles over 10 wt.% Ce-doped catalysts relative to 20 wt.% Ce-doped catalyst was registered and homogeneous distribution of Ce was found on 20 wt.% Ce-doped catalyst. The combined effects led to the lowest Ni/Si ratio obtained on the 10Ni/10Ce/SBA-16 catalyst. In Fig.6.21d, the Ce3d peaks were divided into 10 peaks using the deconvolution method labeled as u and v, and the molar ratio of Ce³⁺ species was calculated [332,426,427,437]. As shown in Table 6.8, the binding energy of Ce3d on 10Ni/20Ce/SBA-16 slightly shifted to a higher energy than those for 10Ni/10Ce/SBA-16. And for Ni species, one could see that the binding energy of Ni2p_{3/2} was higher on 10Ni/10Ce/SBA-16 than on 10Ni/20Ce/SBA-16, showing that the interaction between Ni and Ce is stronger on 10Ni/10Ce/SBA-16 sample. Furthermore, at the surface, the Ce content increased with the Ce loading. However, the Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio is higher on 10Ni/10Ce/SBA-16 than on 10Ni/20Ce/SBA-16, which could be caused by the better dispersion of Ce on the surface and the substitution of Ce by Ni inside the lattice, leading then to more oxygen vacancies as suggested elsewhere [211,332,361,438].

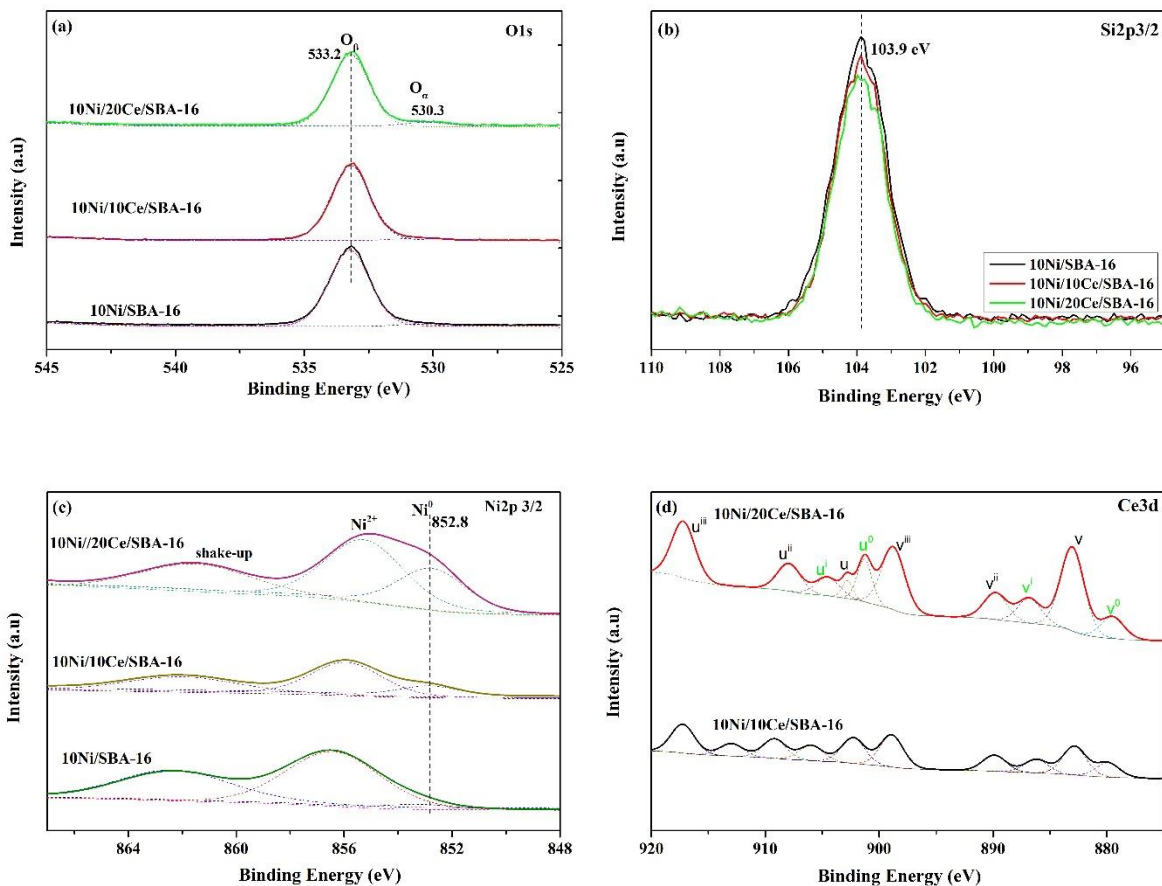


Figure. 6.21. The XPS spectra over the reduced catalysts; Reduction condition: the same as TEM measurement; a) O1s, b) Si2p, c) Ni2p, d) Ce3d

Thus, the promotion of Ni/SBA-16 catalysts by Ce induced the creation of oxygen vacancies, higher dispersion of Ni and Ce on the surface, and stronger metal-support interaction between Ni and Ce formed on 10 wt.% Ce-promoted catalysts compared to 20 wt.% Ce one.

Table 6.8 The binding energies of Ni2p_{3/2} and Ce3d_{5/2} and atomic ratios of Ni (Ni⁰ and Ni²⁺) on the catalysts.

Catalyst	Atomic ratio (%)					Binding Energy (eV)	
	Ce/S	Ni/Si	Ni ⁰ /(Ni ²⁺ +	O _α /(O _α +O _β	Ce ³⁺ /(Ce ³⁺	Ni2p _{3/2}	Ce3d _{5/2}
	i		Ni ⁰))	+Ce ⁴⁺)		
10Ni/SBA-16	-	4.5	4.5	3.3	-	856.4	-
10Ni/10Ce/SBA-16	1.1	3.2	19.7	4.3	35.3	856.0	882.9
10Ni/20Ce/SBA-16	1.4	6.2	36.0	6.3	25.7	855.3	883.1

6.3.1.5 Reducibility of the catalysts originated from H₂-TPR

In order to study the reducibility of supports and catalysts, the temperature-programmed reduction of H₂ was carried out. The plots are displayed in Fig.6.22. The maxima of reduction peak and H₂ consumption of the samples were calculated and presented in Table 6.9. As shown in Fig.6.22a, three reduction peaks of Ce-modified SBA-16 supports can be observed for the xCe/SBA-16 samples. The silica could not be reduced during the employed condition. Thus, the reduction of the supports was attributed to the reduction of Ce species. According to the literature [375,439,440], reduction peaks of 10Ce/SBA-16 at 360-496°C and 757°C in Fig.6.22a were assigned to the reduction of surface and bulk Ce, respectively. As shown in Fig.6.22a, the β and γ peaks of 20Ce/SBA-16 shifted to higher temperature compared to those of 10Ce/SBA-16, indicating that the surface ceria species were more difficult to be reduced over 20Ce/SBA-16, which was in line with the XPS result that more Ce³⁺ formed on 10Ni/10Ce/SBA-16. The total H₂ consumption of 20Ce/SBA-16, as shown in Table 6.9, was also higher than 10Ce/SBA-16. This could be attributed to the more reducible Ce species over 20Ce/SBA-16.

After Ni impregnation, the reducibility of Ni/xCe/SBA-16 catalysts was modified as the incorporation of Ce. As shown in Fig.6.22b, there are three reduction peaks centered at 332, 439, and 584 °C labeled as α , β , and γ , respectively for 10Ni/SBA-16 catalyst. Those reduction peaks located at 332 and 439 °C corresponded to the reduction of NiO crystallites weakly interacted with the SBA-16 support, meanwhile, the reduction peak positioned at 584 °C was attributed to the reduction of Ni phyllosilicate or Ni hydrosilicate species highly dispersed on the surface [389,415,441].

For the Ce-doped Ni/SBA-16 catalysts, H₂ consumption peaks consisted of 5 peaks i.e. δ , α , β , γ and ε (Table 6.9), with two new peaks of δ and ε . Similarly, the peaks of α and β were attributed to the reduction of Ni-Ce biphasic oxides, and the peak of γ corresponded to the reduction of highly dispersed Ni crystallites [389]. The δ peak was attributed to the reduction of adsorbed oxygen species, while the ε peak is attributed to the reduction of Ce⁴⁺ to Ce³⁺ [256,414].

The Ni species can be incorporated into the CeO₂ lattice because of its smaller ion radius, thus the charge unbalances and lattice distortion results in the formation of oxygen vacancies, which are easier for the adsorption of oxygen species [256]. From Fig.6.22b, the peaks of α , β , and γ for Ni/xCe/SBA-16 catalysts showed shifts towards higher temperatures with the increase of Ce loading, indicating the increase of the interaction between metal and support. As shown in Table 6.9, the total H₂ consumption excluding the effect of Ce reduction of the catalysts also increased with the increase of Ce loading, which demonstrates the Ni species are more difficult to be reduced over 20 wt.% Ce-promoted catalysts.

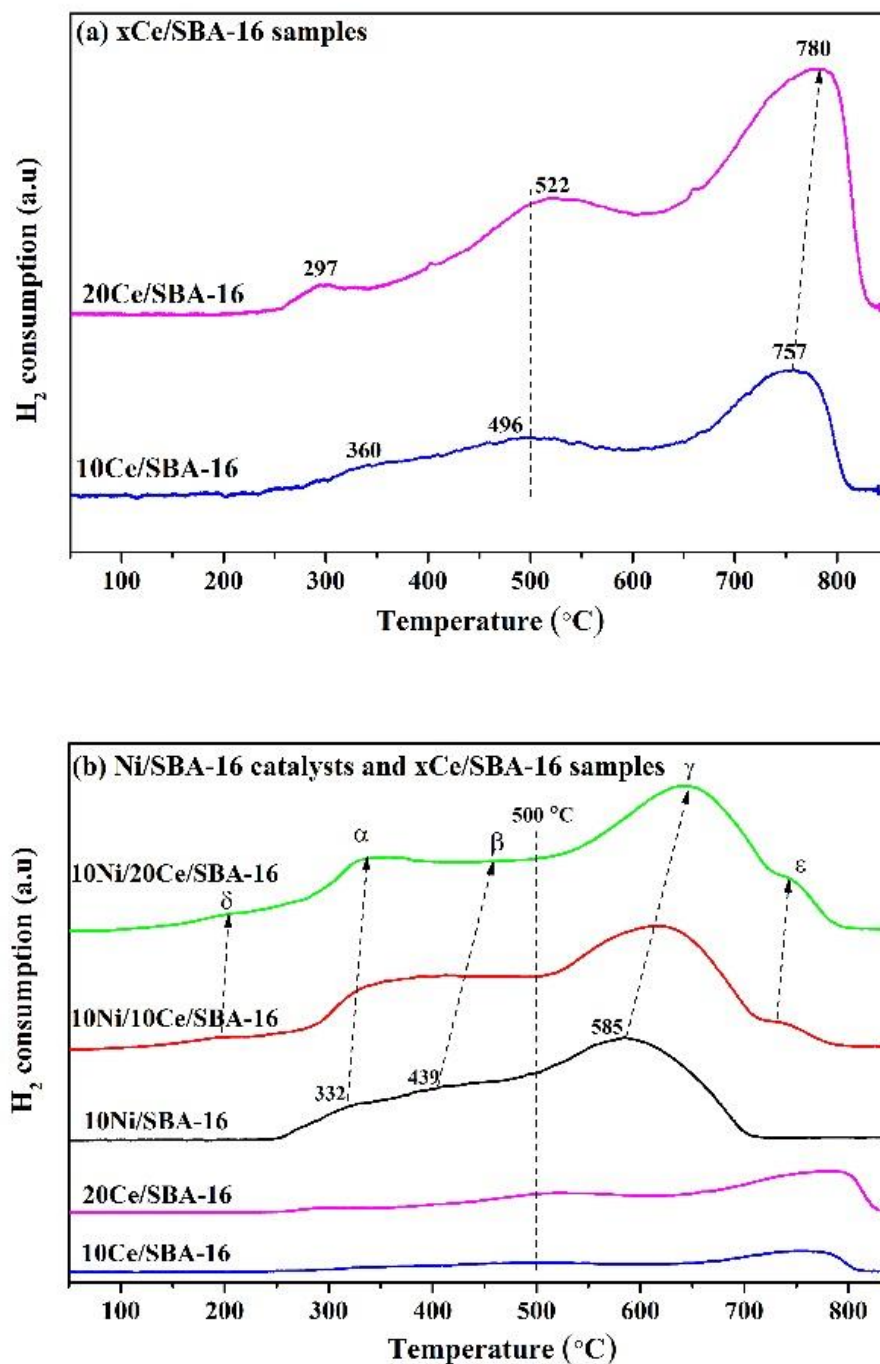


Figure. 6.22. a) H₂-TPR plots of the Ce doped SBA-16 supports; b) H₂-TPR plots of catalysts with xCe/SBA-16 as a comparison.

Table 6.9 H₂ consumption and reduction peaks of the supports and catalysts.

Catalyst	Temperature (°C)					H ₂ consumption (mmol/g)					
	δ	α	β	γ	ε	δ	α	β	γ	ε	total
10Ce/SBA-16	-	359	494	756	-	-	0.01	0.17	0.12	-	0.30
20Ce/SBA-16	-	297	522	781	-	-	0.01	0.29	0.25	-	0.55
10Ni/SBA-16	-	332	439	584	-	-	0.17	0.66	0.63	-	1.46
10Ni/10Ce/SBA-16	206	346	457	617	727	0.05	0.10	0.86	0.99	0.0	2.03
										2	
10Ni/20Ce/SBA-16	210	350	474	642	737	0.05	0.16	1.17	1.01	0.0	2.42
										3	

6.3.1.6 Basicity of the catalysts originated from CO₂-TPD

The CO₂-TPD profiles were displayed in Fig.6.23. Four different desorption peaks of CO₂ can be identified for the 10Ni/SBA-16 catalysts centered at 100, 170, 289, and 650 °C, respectively. The desorption peaks centered at 100 °C, 170-289 °C, and 650 °C were attributed to the weak basic sites, medium basic sites, and strong basic sites, respectively [442]. Since the silica does not adsorb significant amounts of CO₂, it is reasonable to conclude that this activated adsorption occurs only on Ni species of 10Ni/SBA-16 catalyst [165,443].

As displayed in Table 6.10, the total basicity of the catalysts seemed not significantly different, with the highest total basicity obtained over the Ce-free catalyst. This can be attributed to the highly dispersed small Ni metal nanoparticles over the SBA-16 support, as confirmed in TEM, which adsorbed large amounts of CO₂ [443]. For Ce-doped catalysts, the adsorbed CO₂ could be assigned to the adsorption of Ni metal and the active sites of Ce. The introduction of Ce affected

the distribution of basic sites. The number of medium basic sites of Ce-doped catalysts was higher than that of the Ce-free sample. The highest amount of medium basic sites was obtained on the 10Ni/10Ce/SBA-16 catalyst. As reported in the literature [160,206], medium basic sites played a more important role in the CO₂ methanation process and the strong basic sites did not participate in the reaction. The number of medium basic sites was as follows: 10Ni/10Ce/SBA-16 > 10Ni/20Ce/SBA-16 > 10Ni/SBA-16, which can also explain the differences in catalytic activity for CO₂ conversion.

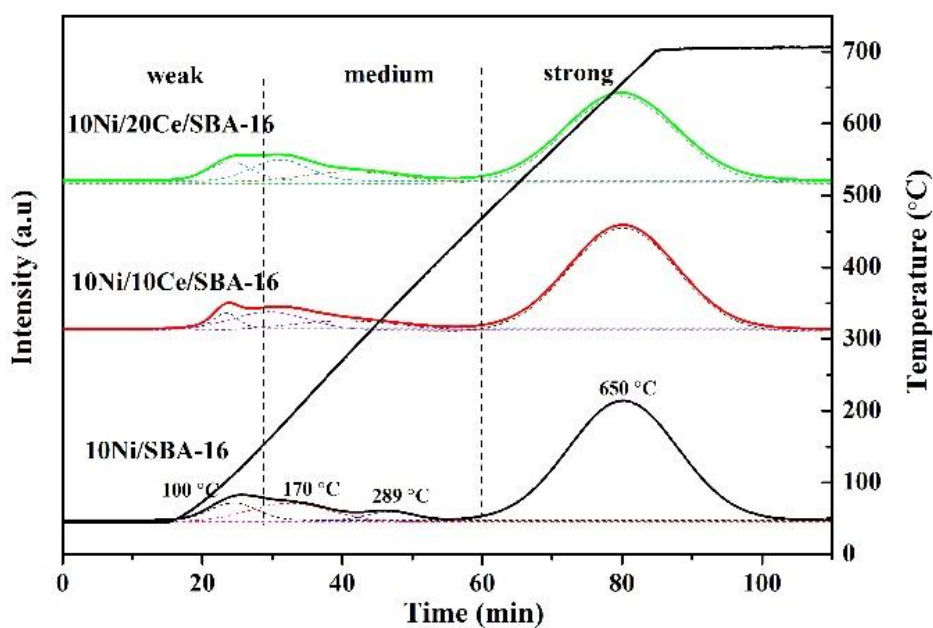


Figure. 6.23. CO₂-TPD curves of Ni/SBA-16 catalysts with or without Ce.

Table 6.10 Basic sites distribution calculated from CO₂-TPD for Ni/SBA-16 based catalysts after reduction at 500 °C

Catalyst	Basic sites [$\mu\text{mol/g}$]				Distribution of basic sites [%]		
	Weak	Medium	Strong	Total basicity	Weak	Medium	Strong
10Ni/SBA-16	14.1	33.5	245.0	292.6	4.8	11.5	83.7
10Ni/10Ce/SBA-16	6.3	43.4	210.0	259.7	2.4	16.7	80.9
10Ni/20Ce/SBA-16	14.6	40.8	181.9	237.3	6.2	17.1	76.7

6.3.1.7 Catalytic tests of the catalysts in CO₂ methanation reaction

The catalytic performances of the catalysts in CO₂ methanation were investigated as a function of temperature. The results are displayed in Fig.6.24. The thick lines without a symbol on the top of the graphs represented the theoretical thermodynamic CO₂ conversion and CH₄ selectivity. From Fig.6.24a, it can be seen that the CO₂ conversions of the catalysts followed the order: 10Ni/SBA-16 < 10Ni/20Ce/SBA-16 < 10Ni/10Ce/SBA-16 at the range of 250-350 °C. At higher temperatures (400 °C), for all samples, CO₂ conversions reached nearly the same value. Then at 450 °C, CO₂ conversions of all catalysts were nearing the theoretical values. From Fig.6.24b, the CH₄ selectivity of all the catalysts increases with the increase of temperature and reaches the highest value at 400 °C, which is nearly the theoretical value, then slightly decreases at 450 °C. The CH₄ selectivity on Ce-modified catalysts is significantly higher than that of Ce-free catalyst at the range of 200-350 °C, but they are similar from 400 to 450 °C. The selectivity of 10Ni/10Ce/SBA-16 was also slightly higher than those obtained on 10Ni/20Ce/SBA-16 at all temperatures except 250 °C. At

350 °C, the best CO₂ conversion and highest CH₄ selectivity are obtained over 10Ni/10Ce/SBA-16. Thus, one can conclude that the 10 wt.% of Ce loading is appropriate content for Ce-doped Ni/SBA-16 catalysts for CO₂ methanation.

According to the literature [161,443], the Ni particle size significantly affected the CH₄ selectivity of silica-supported Ni catalysts in CO₂ methanation reaction. The small Ni particles could favor the formation of CO and the turnover frequency of CO formation. As for Ni/SBA-16 catalyst, in the current study, the active sites are mainly Ni metal sites, thus, the smaller Ni particle sizes favor the formation of CO, thus resulting in the poor CH₄ selectivity at a low-temperature range (<350 °C). But the CH₄ selectivity increases with the increase of temperature and reaches as high as Ce-promoted catalysts at 400 °C, which is attributed to the hydrogenation of CO to CH₄, in which CO played as an important intermediate [161].

However, in the presence of Ce for the Ni/xCe/SBA-16 catalysts, the methanation reaction pathway changes as the Ce actively participates in the reaction [159,224]. In such case, the SBA-16 support plays only as a skeleton to stabilize and disperse the Ni and Ce species, and the catalytic performance is determined by the combined effects of Ni and Ce species, which had also been demonstrated in other catalytic conversions of CO₂ reactions over SBA-16, SBA-15 or KIT-6 mesoporous silica materials supported catalysts [50,171,224,389]. The high dispersion of Ni and Ce species was obtained over 10Ni/10Ce/SBA-16 catalyst, resulting in easily reducible Ni and Ce species as confirmed by TPR characterization. Moreover, more molar ratio of Ce³⁺/(Ce³⁺+Ce⁴⁺) obtained over 10Ni/10Ce/SBA-16, indicating more created oxygen vacancies over the catalyst, which can effectively activate CO₂ in the reaction [160,196,211,332,350]. In this CO₂ methanation pathway, the CO was only a main by-product that originated from the decomposition of formate intermediates over Ce³⁺ sites [211,350]. The CO₂ species adsorbed over Ce³⁺ sites showed different

desorption behaviors over catalysts as revealed in CO₂-TPD, forming different basic sites, in which the weak and moderate basic sites played a significant effect in the reaction [144,160,206,444].

The Ni metal active sites were contributed to the activation and decomposition of H₂, thus, the small Ni particles could provide more sites for the activation of H₂ [211,445]. Compared to 20 wt.% Ce-doped catalyst, the smaller Ni particles of 10 wt.% Ce doped catalyst, as shown in HRTEM, could be more favorable in H₂ activation.

The synergistic effect between Ce and Ni promotes the formation of CH₄. The interaction between Ce and Ni was higher over 10Ni/10Ce/SBA-16 than over 10Ni/20Ce/SBA-16, resulting in the better CO₂ conversion over 10Ni/10Ce/SBA-16.

In Fig.6.25 and Fig.6.26, correlating the catalytic performance with $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ and medium basic sites, it was found that 10Ni/10Ce/SBA-16 showed the best CO₂ conversion at 350 °C with the highest ratio of $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ and the amount of medium basic sites.

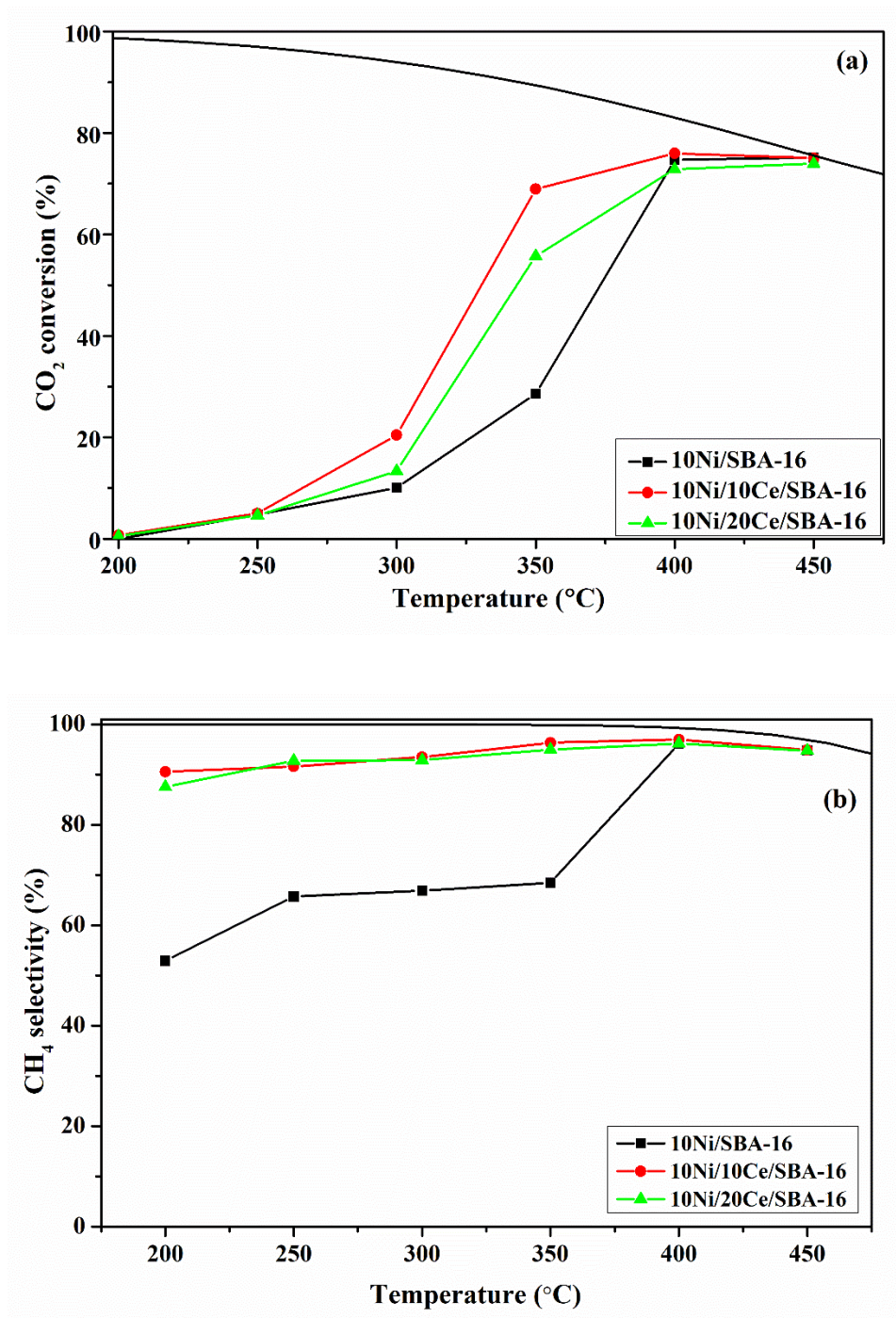


Figure. 6.24. The catalytic performances of Ni/SBA-16 catalysts with or without Ce in CO₂ methanation; a) CO₂ conversion, b) CH₄ selectivity

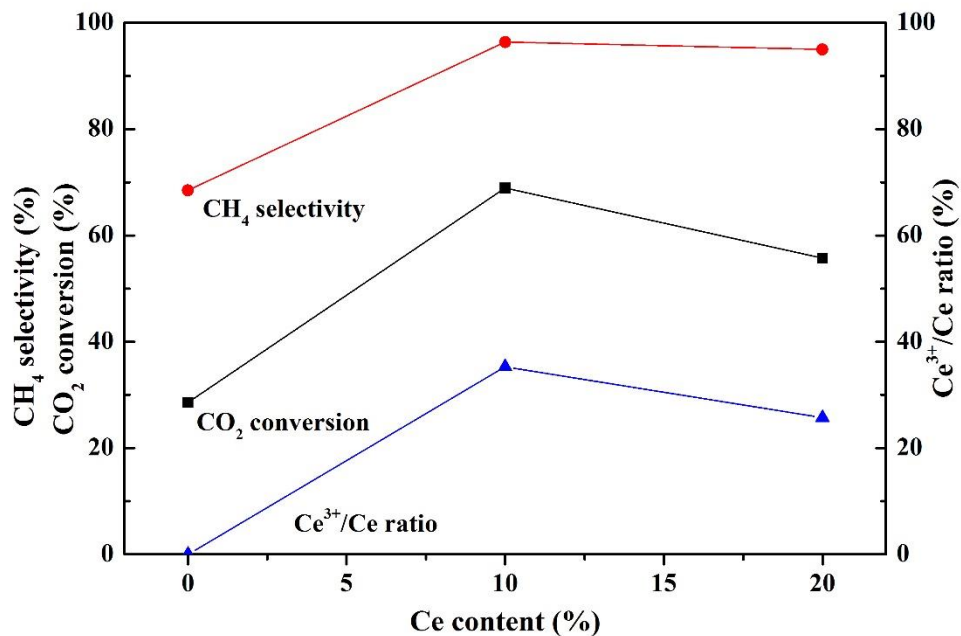


Figure. 6.25. The correlation of CO₂ conversion and CH₄ selectivity at 350 °C with regard to the surface Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio calculated from XPS; The sample of 0 wt.% Ce loading represents the 10Ni/SBA-16 sample.

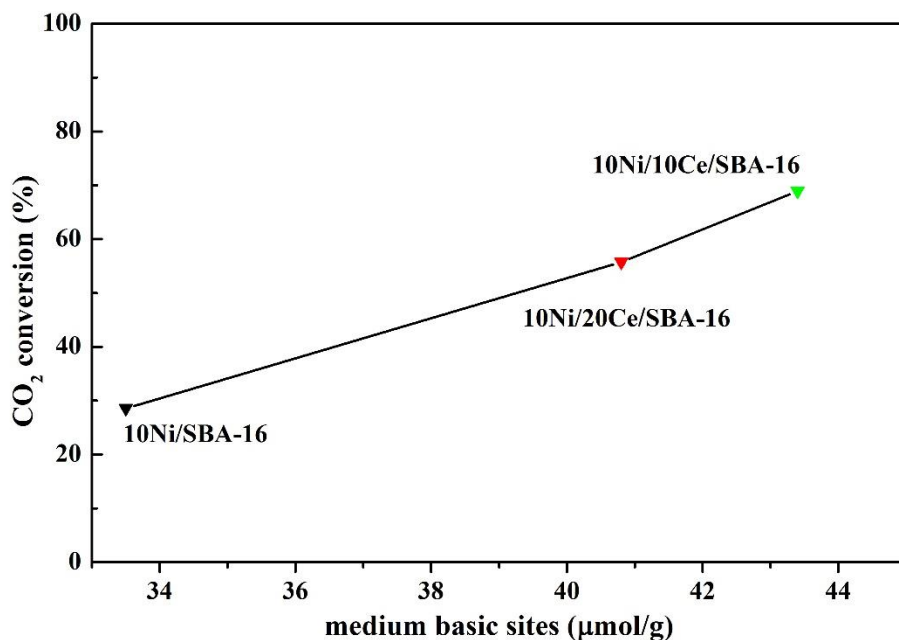


Figure. 6.26. The correlation of CO₂ conversion at 350 °C with medium basic sites.

6.3.1.8 Stability tests of the catalysts in CO₂ methanation reaction

The stability tests of the catalysts in CO₂ methanation reaction were performed and the results were displayed in Fig.6.27. As shown in Fig.6.27, the 10Ni/SBA-16 and 10Ni/10Ce/SBA-16 catalysts all show good stability regarding CO₂ conversion and CH₄ selectivity in the time on stream process. The good stability of Ni/SBA-16 catalysts could be attributed to the confinement of the SBA-16 structure, which can suppress the sintering of active sites [389].

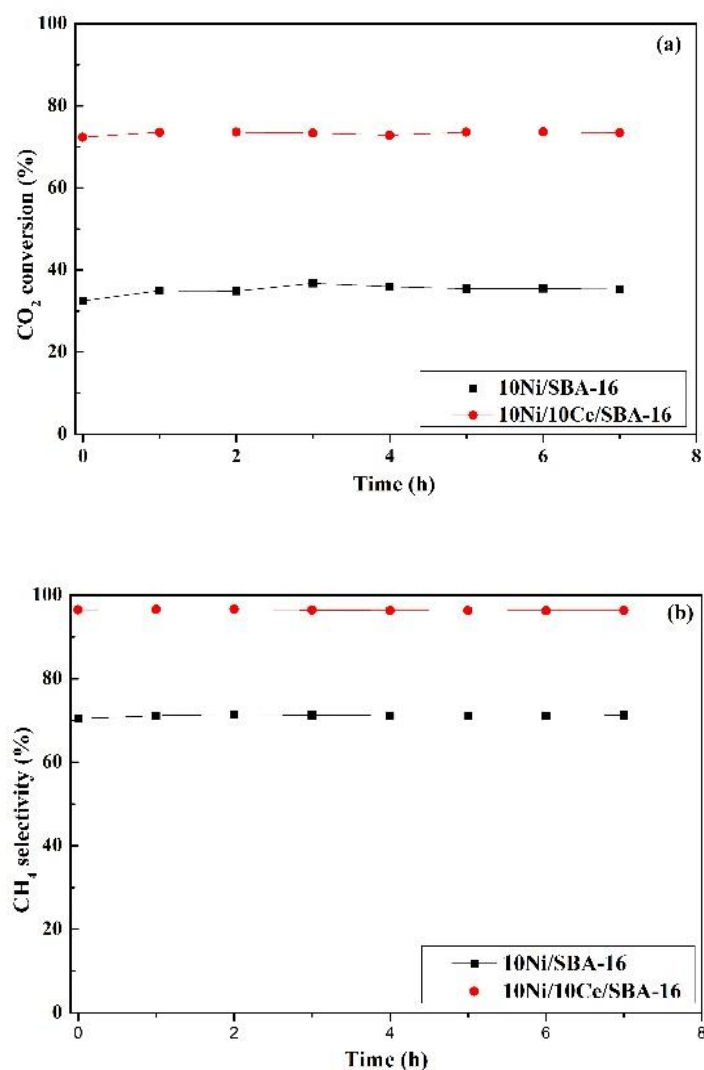


Figure. 6.27. The stability tests of 10Ni/SBA-16 and 10Ni/10Ce/SBA-16 catalysts in CO₂ methanation; Condition: 350 °C, GHSV=12,000 h⁻¹; a) CO₂ conversion, b) CH₄ selectivity.

6.3.1.9 XRD patterns of the catalysts after methanation test

As shown in Fig.6.28, the diffraction peaks of Ni or Ce on spent catalysts remained stable as compared to those on reduced catalysts, indicating that no sintering occurs after time on stream of 7 h.

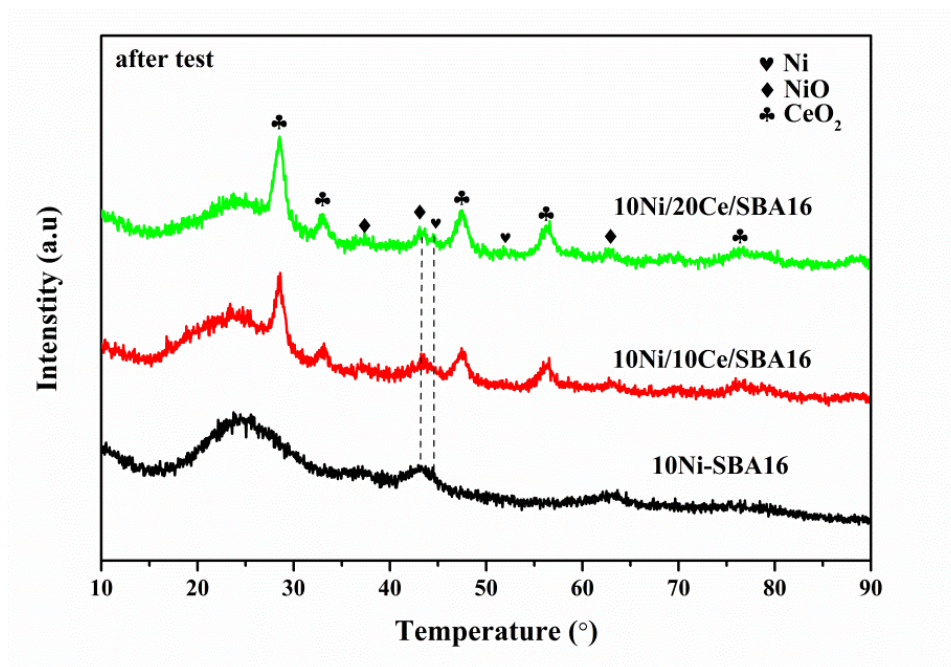


Figure.6.28. XRD patterns of the spent Ni/SBA-16 based catalysts with varying Ce loading.

6.3.1.10 The selection of pre-treatment temperature and Ce loading based on activity test

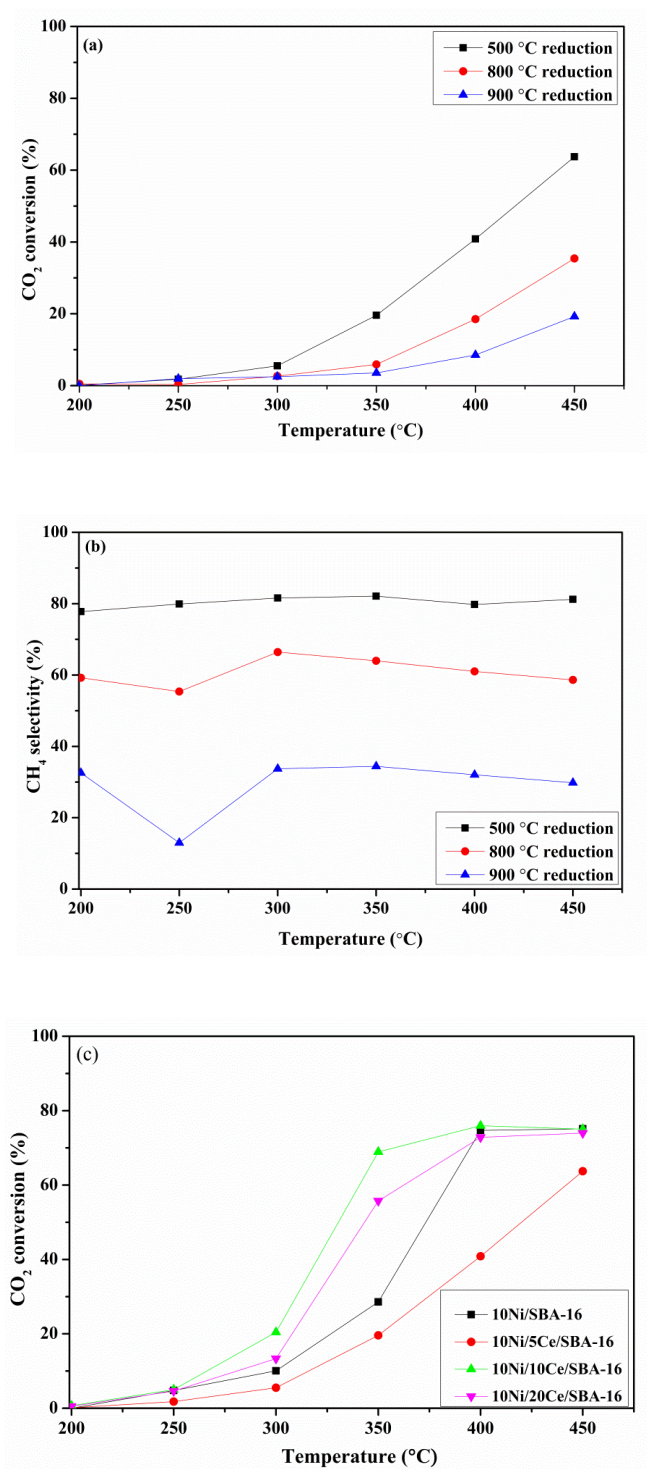


Figure. 6.29. The CO₂ methanation test of 10Ni/5Ce/SBA-16 catalyst reduced at different temperatures; a) CO₂ conversion (%), b) CH₄ selectivity (%)

As shown in Fig.6.29c, the 5 wt.% Ce modified Ni/SBA-16 catalyst shows a worse activity compared to other catalysts at the testing temperature range. In Fig.6.29a and b, it also can be seen that the activity and CH₄ selectivity decrease with the increase of reduction temperature until 900 °C. Thus, it can be concluded that 10 wt.% Ce is appropriate content for Ce-promoted Ni/SBA-16 catalyst in CO₂ methanation and 500 °C is the best condition for the reduction process.

6.3.1.11. Comparison of the Ni/Ce/SBA-16 and Ni/CeY/SBA-16 catalysts in CO₂ methanation.

A series of Ni/CeY/SBA-16 catalysts prepared by citric acid-assisted impregnation method as depicted in 3.1.4.5 of chapter 3. The catalysts were pretreated at 650 °C under 5% H₂/Ar flow for 1 h. The catalytic performance of catalysts was displayed in **Fig.6.30**.

As shown in **Fig.6.30**, the CO₂ conversion and CH₄ selectivity of Ni/Ce/SBA-16 catalyst were improved after doping Y in which 5 wt.% of Y showed the best promotion effect.

However, the Ni/Y/SBA-16 catalyst performs comparative activity as compared to Ni/CeY/SBA-16 catalyst. In such a case, it is interesting to study the effect of Y on Ni/SBA-16 catalyst, which will be discussed in the next sub-chapter.

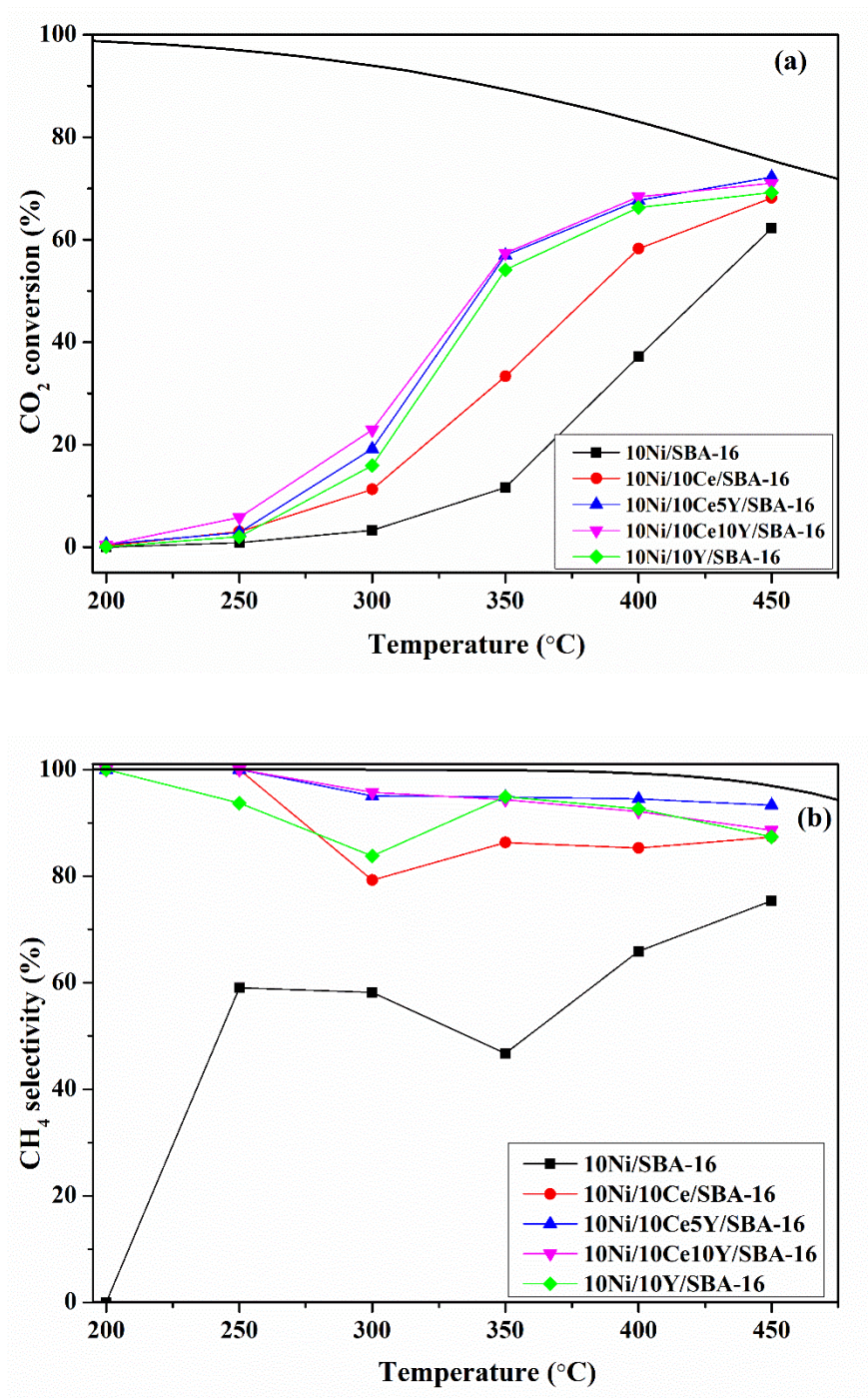


Figure. 6.30. The catalytic performance of Ni/CexY/SBA-16 catalysts in CO₂ methanation; Condition: 650 °C reduced for 1 h, GHSV=12,000; (a) CO₂ methanation, (b) CH₄ selectivity.

6.3.1.12 Conclusions

In this study, the SBA-16 material with cage-type mesopores was successfully synthesized and used to prepare Ni/SBA-16 based catalysts for CO₂ methanation. The effects of Ce promoter on the physic-chemical properties and catalytic performance of the catalysts were studied. It was found that the cage-type mesopores of the SBA-16 matrix, which could suppress the moving and sintering of active metals, leading to good dispersions of active metals. The smallest Ni particles were obtained over the Ce-free Ni/SBA-16 catalyst. Meanwhile, the increase of Ce loading led to larger Ni particles inside/outside the matrix. The Ni and Ce particles of catalyst were found to be smaller over 10 wt.% Ce-doped Ni/SBA-16 catalyst than over 20 wt.% Ce-doped catalyst. Besides, the dispersion degree of Ce decreased over 20 wt.% Ce-doped catalyst and aggregates of Ce were also registered. Moreover, a higher $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$ ratio formed on the surface of 10 wt.% Ce-doped Ni/SBA-16 catalyst, favoring the activation and hydrogenation of CO₂ species adsorbed Ce^{3+} active sites. Furthermore, the highest number of medium basic sites was obtained over 10 wt.% Ce-doped Ni/SBA-16 catalyst, which was favorable for the formation of CH₄. Besides, the stronger Ni-Ce interaction was also formed over 10 wt.% Ce-doped Ni/SBA-16 catalyst.

In the CO₂ methanation, the CO₂ conversion and CH₄ selectivity of Ni/SBA-16 catalyst were lower than Ni/xCe/SBA-16 catalysts at low temperatures, which could be assigned to the lack of active sites for CO₂ activation, which resulted in the CO₂ species adsorbed on Ni/SBA-16 catalyst were easily converted to CO, leading to poor conversion and selectivity. The highest CO₂ conversion and CH₄ selectivity were obtained over 10 wt.% Ce-doped Ni/SBA-16 catalyst due to several advantages relative to 20 wt.% Ce-doped catalysts, such as the smaller particles of Ni and Ce, stronger Ni-Ce interaction, higher molar ratio of $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$, more oxygen vacancies, and more medium basic sites.

In brief, the SBA-16 is appropriate support for Ni catalysts dedicated to CO₂ methanation. Also, Cerium is a good additive to improve Ni/SBA-16 catalyst. Besides, other promoters e.g., Y can also be interesting to modify Ni/SBA-16 catalyst, which will be discussed in the next chapter.

6.4 SBA-15 versus SBA-16: a comparison of the catalytic properties

6.4.1 Comparison of SBA-15 and SBA-16 supported catalysts in CO₂ hydrogenation

Table 6.11 presents the activity in methanation on the different supported materials, performed at 350 °C and 400 °C after steady-state.

Table 6.11 A summary of SBA-15 and SBA-16 supported catalysts in the presence of promoter.

Catalyst	CO ₂ conversion (%)		CH ₄ selectivity (%)	
	350 °C	400 °C	350 °C	400 °C
15Ni/SBA-15	5.5	20.0	35.4	48.3
15Ni10Y/SBA-15	18.0	62.4	87.7	88.0
15Ni10Ce/SBA-15	40.0	68.6	92.5	92.3
15Ni10Ce10Y/SBA-15	61.2	70.6	95.9	94.5
10Ni/SBA-16-WI ^b	28.6	74.7	68.5	96.2
10Ni/10Ce/SBA-16-WI	68.9	76.0	96.4	97.0
10Ni/10Y/SBA-16-CA ^a	54.1	66.3	94.9	92.6
10Ni/10Ce/SBA-16-CA	33.4	58.3	86.3	85.3
10Ni/10Ce10Y/SBA-16-CA	57.4	68.4	94.3	92.1

^a Wet impregnation (ethanol)

^b Citric acid assisted impregnation.

In **Table 6.11**, the activity and selectivity of Ni/SBA-15 and Ni/SBA-16 catalysts were listed. It can be concluded that Ni/SBA-16 shows better activity compared with that of Ni/SBA-15. Also, the performance of Ni/SBA-15 can be improved by doping Ce and/or Y in which the Ce-Y doped Ni/SBA-15 shows the best performance.

Both Ce and Y have shown a positive effect on the performance of Ni/SBA-16 catalyst in which Ce promoted Ni/SBA-16 catalyst prepared by wet impregnation shows the best performance. However, for citric acid-assisted impregnation prepared catalysts, the Y-doped Ni/SBA-16 catalyst performs comparative activity compared to the Ce-Y doped Ni/SBA-16 catalyst. The different activities can be linked with surface properties, basicity, the particle size of the catalysts as presented below.

6.4.2 On the basicity properties: SBA-15 versus SBA-16 supported catalysts

Table 6.12 presents the basic properties measured by CO₂ TPD on the different supporting materials.

As reported in **Table 6.12**, the basicity distribution of SBA-15 and SBA-16 supported catalysts were listed. The promotion with Ce and Y can change the basic site distribution of Ni/SBA-15 catalysts. As observed, Y can promote the increase of medium basic sites with a subsequent decrease of strong basic sites. Cerium can significantly promote the increase of total basic sites of Ni/SBA-15. Finally, Ce-Y can promote the formation of even more medium basic sites.

As for Ni/SBA-16 catalysts, Ni/SBA-16 shows more basic sites compared to Ni/SBA-15 and the presence of Ce promotes the increase of medium basic sites.

Table 6.12 Basicity comparison of SBA-15 and SBA-16 supported catalysts

Catalyst	Basic sites ($\mu\text{mol/mg}$)			
	weak	medium	strong	Total
15Ni/SBA-15	15.8	10.2	8.3	34.3
15Ni10Y/SBA-15	15.2	16.0	3.3	34.4
15Ni10Ce/SBA-15	2.61	47.47	174.45	224.53
15Ni10Ce10Y/SBA-15	4.87	65.94	150	220.81
10Ni/SBA-16-WI	14.1	33.5	245.0	292.6
10Ni/10Ce/SBA-16-WI	6.3	43.4	210.0	259.7

To conclude, the Ni/SBA-16 presents more basic sites compared to that of the Ni/SBA-15 catalyst. Doping with a promoter such as Ce, Y, and Ce-Y can thus promote the basicity of the SBA-15 supported Ni catalysts.

6.4.3 Ni particle size comparison between SBA-15 and SBA-16 supported catalysts

Table 6.13 reports the particle size calculated from the Scherrer equation from XRD on the different supported calcined materials.

Table 6.13 shows the particle size of NiO of SBA-15 and SBA-16 supported catalysts. It can be seen that the promotion by Ce, Y, and Ce-Y lead to the decrease of NiO particle size of Ni/SBA-15. For SBA-16 supported catalysts, the presence of Ce leads to a slight increase in NiO particle size. The media NiO particle size of Ni/SBA-16 with/without Ce is smaller than that of Ni/SBA-15 catalysts.

Table 6.13 Particle size of the calcined samples from XRD

Catalyst	Ni particle size (nm) ^a
15Ni/SBA-15	18.0
15Ni10Y/SBA-15	14.5
15Ni10Ce/SBA-15	13.4
15Ni10Ce10Y/SBA-15	15.3
10Ni/SBA-16-WI	4.3
10Ni/10Ce/SBA-16-WI	7.7

Table 6.14 presents the particle size calculated from the Scherrer equation from XRD on the different supported reduced materials.

Table 6.14 Particle size of the reduced samples from XRD

Catalyst	Ni metal particle size (nm) ^a
15Ni/SBA-15	24.1
15Ni10Y/SBA-15	16.0
15Ni10Ce/SBA-15	19.5
15Ni10Ce10Y/SBA-15	21.0
10Ni/SBA-16-WI	6.4
10Ni/10Ce/SBA-16-WI	7.2

As shown in Table 6.14, the largest Ni metal particle was found on 15Ni/SBA-15 catalyst. The Ni metal particle size was smaller when Y, Ce, or Ce-Y was added. Compared to 15Ni10Ce/SBA-15, the particle size of Ni metal increased slightly.

As for SBA-16 supported catalysts, the particle size of Ni metal is much smaller than that of SBA-15 supported catalysts. Doping Ce leads to a slight increase of Ni metal particle size over 10Ni/10Ce/SBA-16-WI catalyst.

6.4.4 Surface atom ratio comparison from XPS between SBA-15 and SBA-16 supported catalysts

By XPS, the surface comparison of both Ni supported SBA-15. And SBA-16 catalysts were evaluated. The results are presented in Table 6.15.

Table 6.15 Surface composition of the reduced catalysts from XPS

Catalyst	Atomic ratio (%)					
	Ni	Ce	Y	Ni ⁰ /Ni ²⁺	O _{OH} /O	Ce ³⁺ /(Ce ³⁺ + Ce ⁴⁺)
15Ni10Ce/SBA-15	1.1	0.6	-	21.8	9.0	48.2
15Ni10Ce10Y/SBA-15	1.2	0.5	4.8	11.7	23.9	57.2
10Ni/SBA-16-WI	0.8	-	-	4.7	3.3	-
10Ni/10Ce/SBA-16-WI	0.08	0.01	-	24.5	4.3	35.3

Table 6.15 shows the surface composition of reduced catalysts. It can be noted that the surface atom ratio of Ni and Ce on SBA-15 support is higher than on SBA-16 support.

The highest Ni⁰/Ni²⁺ ratio was found on the 10Ni/10Ce/SBA-16 catalyst. Thus, this can explain that such catalysts are active in methanation since the Ni⁰ species are well known to be the active site in the methanation reaction [232].

On the contrary, the highest surface adsorbed oxygen species and highest Ce³⁺ ratio was found on 15Ni10Ce10Y/SBA-15 catalyst. Thus, on this support, the importance of the oxygen vacancies led to high activity in methanation [366].

Thus, it is worth noting that depending on the support 2D or 3D structure, the surface properties have changed.

6.5 Conclusion

Ni catalysts supported on SBA-15 and SBA-16 are promising catalysts due to their high SSA, pore volume, and unique ordered mesostructure. It was shown here, that the presence of Ce or Y can promote the activity of Ni/SBA-15 catalysts in CO₂ methanation. Meanwhile, the Ce-Y promoted Ni/SBA-15 catalyst showed the best activity.

Compared to SBA-15, SBA-16 can be better alternative support for Ni catalysts due to its three-dimension mesoporous structure. Ni/SBA-16 showed the smallest Ni particle size and high dispersion of Ni. In the presence of Ce, the medium basic sites and Ce³⁺ ratio increased over Ni/SBA-16-Ce, which resulted in higher activity.

Although the Ce-Y promoters can promote the activity of the Ni/SBA-16 catalyst, the Y doped Ni/SBA-16 catalyst shows comparative activity. Thus, it can be interesting to study the effect of the only Y on the catalytic performance of the Ni/SBA-16 catalyst.



Chapter VII

Conclusion and perspectives of this work

VII Conclusion and perspective of this work

7. Conclusion and perspectives of this work

7.1 Conclusion

In the first part of this work, low-cost materials such as diatomite and LDHs were employed to synthesize Ni catalysts. The effect of nickel salts on the performance of Ni catalysts in CO₂ methanation was investigated by H₂-TPR, CO₂-TPD, N₂ physisorption, and XRD technologies. It was found that Ni-Mg catalyst derived from nickel nitrate presented the best activity and selectivity, which could be ascribed to the small Ni⁰ particle, good reducibility, and the highest medium basic sites. However, the activity of diatomite-based Ni catalysts seems not satisfactory. Thus, the diatomite-supported catalysts still need more research to improve the activity in CO₂ methanation.

As for LDHs derived Ni catalysts, the effect of Y on the performance of Ni catalysts was studied. It was found that the addition of Y affected the CO₂ adsorption capacity of the materials by changing the distribution of the basic sites, especially those of medium strength. The yttrium promotion influenced the nickel/support interaction. The Y addition affected strongly the catalytic activity in CO₂ methanation, increasing the CO₂ conversion at 250 °C from 16% for MO-0Y to 40 and 81% for MO-2.0Y and MO-0.4Y, respectively. This could be explained by both increased distribution of medium-strength basic sites and significantly smaller metallic nickel particle size of Y-promoted catalysts.

The mixed oxides Ni catalysts derived from LDHs showed high activity and selectivity in CO₂ methanation. The yttrium promoter showed highly improved performance for mixed oxides Ni catalysts.

In the second part, the CeO₂ nanoparticles doped by Y were synthesized by the hydrothermal method and employed to prepared Ni catalysts. The catalysts were studied in CO₂ methanation and

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characterized by a series of physicochemical technologies. The catalytic test showed that doping Y could significantly improve the activity of the Ni/CeO₂ catalyst. In the range of 250-350 °C, the Ni/CeO₂-Y catalysts showed high activity and CH₄ selectivity. By characterization, it was found that the specific surface area of Ni/CeO₂-Y samples, the crystallite sizes of ceria, the oxygen vacancies content, and the interaction between NiO and CeO₂ can be tuned by different Y content.

All the catalysts contain well-defined Ni crystallites and the introduction of Y tailors the particle sizes and shapes of CeO₂ in the catalysts. Unpromoted CeO₂ particles are large nano-cubes turning to nanorods by Y promotion, with an increase of these nanorods size of up to 2 wt% of Y addition.

Highly dispersed Ni active sites in strong interaction with the ceria-based oxide and the oxygen vacancies formed by Y addition are the key factors determining high catalytic activity and stable performances of the Ni/CeO₂-Y catalysts.

The Ni/CeO₂-Y 2.0% with the highest number of oxygen vacancies able to activate CO₂ and with the strongest metal-support interaction suppressing sintering of the Ni sites for H₂ activation, was the best performing CO₂ methanation catalyst.

In the third part, two different mesoporous silica SBA-15 and SBA-16 were synthesized and used to prepare Ni catalysts. The effect of yttrium promotion on SBA-15-supported Ni-Ce catalysts was also investigated on these catalysts for CO₂ methanation. The microscopy analyses (TEM, HRTEM, EDS) revealed that modification with Y positively affects the distribution of Ni particles, being extensively dispersed inside the mesoporous channels of SBA-15 silica support. Moreover, as shown by XPS, yttrium as a promoter contributed to an increase of Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio and the number of medium basic sites, enhanced the reducibility of nickel species, and led to the formation of a Y-Ce solid solution. NiCeY/SBA-15 catalysts showed better catalytic performance

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in CO₂ methanation than Y-free catalyst, with the highest CO₂ conversion and CH₄ selectivity measured for 10 wt.% Y loading. Meanwhile, 15Ni10Ce10Y/SBA-15 showed excellent coking resistance and anti-sintering ability, which can be attributed to the confinement of the SBA-15 structure. However, although increases of activity and selectivity of Ni/SBA-15 catalysts doped by yttrium were found, they were lower compared with Ce and Ce-Y doped NiCe_xY/SBA-15 catalysts.

The effects of Ce promoter on the physical-chemical properties and catalytic performance of the Ni/SBA-16 catalysts were investigated. It was found that the cage-type mesopores of the SBA-16 matrix, which could suppress the moving and sintering of active metals, leading to good dispersions of active metals. The smallest Ni particles were obtained over the Ce-free Ni/SBA-16 catalyst. Meanwhile, the increase of Ce loading led to larger Ni particles inside/outside the matrix. The Ni and Ce particles of catalyst were found to be smaller over 10 wt.% Ce-doped Ni/SBA-16 catalyst than over 20 wt.% Ce-doped catalyst. Besides, the dispersion degree of Ce decreased over 20 wt.% Ce-doped catalyst and aggregates of Ce were also registered. Moreover, a higher Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio formed on the surface of 10 wt.% Ce-doped Ni/SBA-16 catalyst, favoring the activation and hydrogenation of CO₂ species adsorbed Ce³⁺ active sites. Furthermore, the highest number of medium basic sites was obtained over 10 wt.% Ce-doped Ni/SBA-16 catalyst, which was favorable for the formation of CH₄. Besides, the stronger Ni-Ce interaction was also formed over 10 wt.% Ce-doped Ni/SBA-16 catalyst.

In the CO₂ methanation, the CO₂ conversion and CH₄ selectivity of Ni/SBA-16 catalysts were found lower than for Ni/xCe/SBA-16 catalysts at low temperatures. This latter result could be assigned to the lack of active sites for CO₂ activation, which resulted in the CO₂ species adsorbed on Ni/SBA-16 catalyst were easily converted to CO, leading to poor conversion and selectivity.

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The higher CO₂ conversion and CH₄ selectivity (<350 °C) were obtained over 10 wt.% Ce-doped Ni/SBA-16 catalyst due to several advantages relative to 20 wt.% Ce-doped catalysts, such as the smaller particles of Ni and Ce, stronger Ni-Ce interaction, higher molar ratio of Ce³⁺/(Ce³⁺+Ce⁴⁺), more oxygen vacancies, and more medium basic sites.

7.2 Perspectives

In CO₂ methanation reaction, Ni particle size, high surface area, high pore volume, good basicity, enhanced Ni-support interaction, and high oxygen vacancies, etc. can significantly affect the activity and CH₄ selectivity of Ni catalysts. The support and promoter have an important influence on such aspects. Based on the results of this work, several perspectives can be listed as follows:

- The low-cost materials can be competitive in future industrialization. Diatomite-supported Ni catalysts need further improvement. LDHs derived Ni catalysts showed high activity and selectivity making them promising alternatives toward large-scale application.
- Yttrium is an interesting promoter to modify the properties of Ni/CeO₂ catalysts. The solid solution of Y-Ce can be interesting in the study of Y-doped Ni/CeO₂ catalysts.
- SBA-15 supported Ni catalysts showed good stability. However, further improvement researches should be carried out by doping other promoters, changing the preparation method, or modifying the support by ammonia, etc.
- SBA-16 can be good support due to its three-dimension structure and good textural properties. Y-doped Ni/SBA-16 catalysts can be interesting in the next study.

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Annexes

Annex. 1. The titration set-up for precipitation (a) and Polytetrafluoroethylene (PTFE) lined hydrothermal autoclave (b) for syntheses of mesoporous materials.

