



Properties of copper species stabilized in zeolite nanocrystals

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Properties of copper species stabilized in zeolite nanocrystals

**Présentée et soutenue par
Anastasia KHARCHENKO**

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devant le jury composé de**

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To my Family

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Résumé

Il est connu que le progrès social à long terme et la croissance économique, mais aussi la sécurité et la pérennité écologique, nécessitent des alternatives aux carburants et produits chimiques à base de pétrole. Parmi les sources d'énergies renouvelables, la plus abondante est de loin le soleil. Son utilisation pour la production d'énergie requiert une méthode de captage et de stockage.

Le développement des nouveaux matériaux performants ne peut pas être considéré seulement par rapport aux performances des matériaux récemment synthétisés. Donc, de nouvelles méthodes pour la préparation de matériaux de taille nanométrique doivent être développées tout en tenant compte des préoccupations économiques et environnementales mondiales. Ainsi, avec ces idées en tête, le défi de ce travail a été de préparer des nanomatériaux de zéolithe contenant du métal tout en étant fortement actifs, sélectifs, stables, robustes et peu coûteux. Le cuivre a été choisi, en tant que métal non-noble abondant, de par sa haute conductivité, ses propriétés catalytiques et son faible coût. Les zéolithes contenant du cuivre suscitent un vif intérêt de par le prix faible du cuivre et son excellente activité catalytique pour une vaste gamme de réactions, y compris la réduction catalytique sélective de NO, la synthèse et la décomposition du méthanol et d'autres alcools supérieurs, etc. Dans ce travail, des zéolithes de tailles nanométriques ont été utilisées comme hôte pour le cuivre de par leur haute capacité d'échange ionique, grande surface, un système de pores et une topologie réguliers donnant des emplacements définis pour le cuivre. La performance de ces matériaux dans les applications mentionnées ci-dessus dépend de l'emplacement, la coordinence, la réactivité et la mobilité du cuivre dans la charpente zéolithique.

Les objectifs principaux de ce travail étaient d'étudier la nature des composés de cuivre formés dans les nano-zéolithes en utilisant deux approches: (i) incorporation directe du Cu via une synthèse mono pot et (ii) incorporation post-synthèse du Cu suivi par une réduction chimique. Une étude détaillée de l'évolution des espèces de cuivre dans la suspension de nano-zéolithe LTL réduite avec de l'hydrazine a révélé la formation de nanoparticules de cuivre avec des dimensions limitées par la taille de canaux et des cages de la zéolithe. Cependant, avec un temps de réduction prolongé, les NPs de Cu ont tendance à migrer vers la surface de la zéolithe en raison de leur forte mobilité dans les milieux aqueux, et donne lieu à de grosses particules de cuivre, tout en conservant la structure de la zéolithe.

La réduction du cuivre donne lieu à un système complexe contenant différentes espèces de cuivre: des résidus de Cu^{2+} , Cu^+ et des NPs de Cu. Les études par spectroscopie IRTF montrent l'hétérogénéité des cations Cu^{2+} et Cu^+ dans la zéolithe Cu-LTL préparée par échange ionique. Il a été prouvé, que l'état et le comportement du cuivre dans la zéolithe LTL dépendent fortement de la méthode utilisée pour l'incorporation du Cu, soit par échange ionique, soit par incorporation directe du Cu. Il est devenu évident que le cuivre ajouté au mélange de synthèse possède un environnement distinct et occupe une position différente quand il est comparé à celui de l'échange ionique. Il est vraisemblablement partiellement localisé dans la charpente zéolithique ou /caché dans la structure et est inaccessible pour les molécules adsorbées. De plus, les modifications post-synthèse du matériau obtenu par synthèse directe entraînent un déplacement vers des positions hors structure d'un nombre important de Cu.

De plus, les films minces de zéolithes contenant du métal avec des épaisseurs différentes ont été obtenue par un procédé de revêtement par centrifugation de supports de silicium et/ou des supports optiques CaF_2 . Ce dernier a été utilisé pour la détection de CO en faible concentration à température ambiante et l'étude de la réponse optique ultrarapide du matériau photo-excité en résonance avec la bande du plasmon des NPs métalliques.

En résumé, ce travail couvre entièrement toutes les étapes de la synthèse, la modification, la caractérisation complète et l'utilisation de nano-cristaux de zéolithe contenant du métal. La combinaison des propriétés uniques des nanoparticules de cuivre et de la polyvalence des nano-zéolites donne lieu à des matériaux avancés intéressants pour de nombreuses applications dans des dispositifs de taille nanométrique, la détection sélective de produit chimique, la catalyse, etc...

Abstract

It is well recognized that long term social progress and economic growth, as well as security and environmental sustainability, require alternatives to petroleum-based fuels and chemicals. Between the various renewable energy sources, by far the largest resource is provided by the sun. The use of solar energy for energy production requires a capture and storage process.

The development of the new effective materials cannot be only considered based on the efficiency of the lately synthesized materials. Therefore, new methods for preparation of nanosized materials must be developed considering the global economic and environmental concerns. Thus, in the scope of this work the challenge was to prepare metal-containing zeolite nanomaterials that are highly active, selective, stable, robust, and inexpensive. Copper is chosen as an abundant non-noble metal because of its high conductivity, catalytic properties, and low cost. Copper containing zeolites are of great interest due to the low cost of copper and its excellent catalytic activity in a wide range of reactions, including selective catalytic reduction of NO, synthesis and decomposition of methanol and higher alcohols, etc. In this work, nanosized zeolites have been utilized as a host for copper owing to their high ion exchange capacity, large surface area, regular pore systems and topology giving defined locations for copper species. The performance of these materials in the above applications depends on the location, coordination state, reactivity, and mobility of copper species in the zeolite frameworks.

The thesis consists of the five main chapters, literature overview, methods and conclusions. In the introduction the general information about zeolites, nanosized zeolites, their properties, preparation and applications, as well as preparation of metal nanoparticles, in particular, copper, methods of reduction of metal precursors and stabilization are emphasized. The

importance of developing new material, such as zeolite nanocrystals functionalized with copper nanoparticles, for advanced applications are shown.

The methodical part includes the detailed description of materials preparation: LTL type zeolite synthesis, introduction of copper by ion exchange, reduction of copper species, assembly of copper containing zeolites suspensions in thin films and direct incorporation of copper in the zeolite structure. A brief description of all characterization technics used (XRD, SEM, TEM, DLS, N₂ sorption/desorption, TG, ICP-OES, EDX, XPS, NMR, EPR, in situ IR, UV-vis, Raman, Operando, nano indentation) is given in the chapter, as well.

The first chapter entitled “Metal copper nanoparticles in LTL nanosized zeolite: kinetic study” addresses the detailed analysis of preparation of copper nanoparticles with desired properties. The inclusion of copper NPs in the nanosized zeolite matrix is a promising route for the development of advanced materials with improved diffusion within the host combined with chemical reactivity of metal NPs. Copper was introduced to the zeolite host by ion exchange post synthesis method. The results showed the entire preservation of zeolite host after the ion exchange process. Chemical analysis and EDX results showed partial substitution of potassium by Cu (amount of copper was found to be in 1-1.5 wt.%). In addition, it was shown that copper was homogeneously distributed along the zeolite matrix. Stable aqueous suspension of copper exchanged LTL nanozeolite was further reacted by three reducing agents, hydrazine monohydrate, triethylamine and sodium borohydride. With triethylamine no reduction of copper occurred. When NaBH₄ was used there was a rapid reduction leading to formation of big nanoparticles outside the LTL structure, whereas reaction with hydrazine led to slower formation of stable and small nanoparticles. Hence, the system Cu²⁺-LTL/hydrazine was used for further studies. This made possible the investigation of evolution of copper nanoparticles with UV-Vis spectroscopy and TEM technique. The results showed that after 290 minutes of reduction the yield of Cu⁰ species is about 50% and copper nano particles are stable and well

dispersed all over the host matrix with a narrow size distribution from 0.4 – 2.2 nm. While longer reduction leads to the migration of copper towards surface of the hostage with the following growth of large copper particles.

The second chapter entitled “Metal copper nanoparticles in LTL nanosized zeolite: spectroscopic study” is dedicated to the nature and the amount of the copper species introduced in the zeolite framework and their quantification by set of spectroscopic techniques. In order to identify the nature of copper species and to describe their local environment, the samples were examined by means of X-ray diffraction (XRD), ^{29}Si and ^{63}Cu solid state nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), UV-vis spectroscopy, Electron Paramagnetic Resonance (EPR) and high resolution transmission electron microscopy (HRTEM) together with EDX mapping. In addition, to probe the acidity of copper-containing zeolites, temperature programmed desorption of pyridine followed by infrared spectroscopy has been performed. Complementary characterization of Cu-LTL zeolites was also carried out using TEM, N_2 adsorption, DLS and chemical analysis. The investigation of the nature of the copper species proved to be a difficult task that demands multi technique approach. However, it was demonstrated that copper in the final material is present mainly in the Cu^0 , Cu^+ oxidation state and there are reseals of Cu^{2+} species.

In the third chapter “Cu species introduced in nanosized LTL zeolites by in-situ and ion-exchange approaches” the synthesis of a new material is presented, where copper was introduced into a zeolite structure. The incorporation of copper in the zeolite structures with LTL topology has been proved by combination of various technics. X-ray diffraction (XRD) and the Pawley fit of the obtained patterns allowed seeing the changes in the unit cell parameters of the new material in comparison to the parent LTL zeolite. Different sites were probe by Fourier transformed infrared spectroscopy (FTIR) of adsorbed probe molecules (CO, NO), and it was shown that in the sample prepared by direct incorporation of copper, only carbonils and

nitrosils of K^+ were formed. X-ray photoelectron spectroscopy (XPS), ^{29}Si magic angle spinning nuclear magnetic resonance (MAS-NMR) and Electron Paramagnetic Resonance (EPR) allowed determination of the oxidation state and coordination of copper species presented in the zeolite structures. The size of zeolite nanocrystals and copper distribution along the particles were confirmed by high-resolution transmission electron microscopy (HRTEM) combined with EDX mapping. In addition, to probe the acidity of copper-containing zeolites, temperature programmed desorption of pyridine followed by infrared spectroscopy has been performed. The results showed that copper could be partially situated in the structure of the zeolite, however such kind of structure is not stable, and copper tends to leave its position during multi-step post-synthesis treatments, such as ion exchange with ammonium chlorate and calcination.

In the fourth chapter entitled the preparation on various substrates and mechanical properties, such as thickness and roughness, of copper containing zeolite thin films are discussed. Zeolite thin films were used for detection of low concentration of CO at RT. By using Operando IR set-up, it was observed, that Cu-LTL show films high sensitivity and fast response toward low concentrations of CO (1-100 ppm).

The fifth chapter deals with LTL nanosized zeolites used as a host for nm-sized silver NPs. the potential of this material for hot-electrons driven chemistry applications is explored. This issue is addressed by using UV-vis transient absorption spectroscopy, which proved to be a method of choice to characterize the hot-electrons dynamics, and their coupling with the surrounding media. The plasmonic response of silver nanoparticles (Ag NPs) in LTL-type zeolite films under vacuum atmosphere has been investigated. The preparation of Ag NPs in the nanosized LTL- type zeolites, followed by the preparation of the transparent films, and testing of their compatibility with the requirements of the transient absorption spectroscopy are presented. The ultrafast plasmonic response of these materials is reported.

In conclusion, the combination of unique properties of copper nanoparticles with versatility of nanozeolites give rise to the development of advanced materials which are interesting for many applications in nanoscale devices, selective chemical sensing, catalysis etc.

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Literature overview

Introduction

It is well recognized that long term social progress and economic growth, as well as security and environmental sustainability, require alternatives to petroleum-based fuels and chemicals. The consumption of fossil fuels at the actual rate produce a potentially significant global issue resulting from the CO₂ emission. Actual average CO₂ concentration is around 410 ppm (April 2017 from www.co2now.org), whereas climate model predicts more or less moderated global response starting from an average CO₂ concentration equal to 550 ppm. To keep the CO₂ level below 550 ppm, the projected carbon intensity in 2050 is about 0.45 kg of C yr⁻¹ W⁻¹, which is lower than that of any of the fossil fuels. The only way one can reach this value is through a significant contribution of carbon-free power to the total energy mix. There are three main routes for carbon-neutral power: (1) nuclear fission, (2) CO₂ capture and storage, and (3) use of renewable energy. Between the various renewable energy sources, by far the largest resource is provided by the sun. The large gap between our present use of solar energy and its enormous undeveloped potential defines a compelling imperative for science and technology in the 21st century.

In this context, energy efficiency also is identified as a targeted objective to support the development of alternative energy sources as well as to elaborate sustainable chemistry strategies. Hence, the energy requirements of the chemical processes should be recognized for their environmental and economic impacts and have to be minimized. Preferentially, synthetic methods should be conducted at ambient temperature and pressure, for less hazard, more selectivity, biocompatibility, etc. To fulfill these requirements a global strategy should be undertaken, including: better selectivity of the reaction schemes, more efficient catalysts,

reactor size reduction, and selective deposition of the energy (in opposition to the usual global heating practice).

The use of solar energy for energy production requires a capture and storage process. The processes for the solar energy conversion are developed following photovoltaic or photothermal approaches. The photothermal strategy in principle is very simple and based on the absorption of the solar energy by materials to generate heat. The heat can be stored thermodynamically in fluids or materials as energy source for electrical power-plants or converted into chemical energy in the form of solar fuels (solar-to-chemical energy conversion). The key concepts of the solar thermochemical conversion technology are well established.^{1,2}

Besides, alternative thermochemical routes must also be explored to perform solar-to chemical energy conversion under mild conditions, compatible with small-sized local and transportable reactors, and allowing for the exploitation of the water splitting reaction, the ultimate renewable and sustainable energy source. Toward this end, a promising route is the so-called “smart chemistry” that targets the size-reduction concept via the development of nanoreactors and their integration as elementary building units in macroscopic assemblages.

Ultimately, a nanoreactor is a device in which thermodynamics and chemistry are operated at the space scale of the molecular bonds and at the time scale of the molecular motions. Combining such a nanoreactor methodology with a procedure allowing for the local deposition of thermal energy close to the reaction center is expected to be of great importance and need for (i) saving energy and (ii) improving the reaction yield and selectivity by limiting side reactions in confined space (concomitant channels).

The development of the new effective materials cannot be only considered based on the efficiency of the lately synthesized materials. Therefore, new methods for preparation of

nanosized materials must be developed considering the global economic and environmental concerns.

Thus, in the scope of this work the challenge was to prepare metal-containing zeolite nanomaterials that are highly active, selective, stable, robust, and inexpensive. Copper is chosen as an abundant non-noble metal because of its high conductivity, catalytic properties and much lower cost than for instance gold, silver and rhodium.

Copper, a 3d transition metal, is among the 25 most abundant elements in the earth's crust, occurring at an average of about 50–100 g ton⁻¹. Copper metal has played an important role in human technological, industrial, and cultural development since primitive times. Thus, along with iron and gold, copper was one of the first metals used widely.³ Cu-based materials can promote and undergo a variety of reactions due to its wide range of accessible oxidation states (Cu⁰, Cu^I, Cu^{II}), which enable reactivity via both one- and two-electron pathways. Because of their unique characteristics and properties, Cu-based nanocatalysts have found many applications in nanotechnology, including catalytic organic transformations, electrocatalysis, and photocatalysis.⁴ One economical way of creating advanced Cu-based nanomaterials for catalysis is to anchor it on supports such as metal oxides, SiO₂, carbon-based materials, polymers, zeolites.⁴

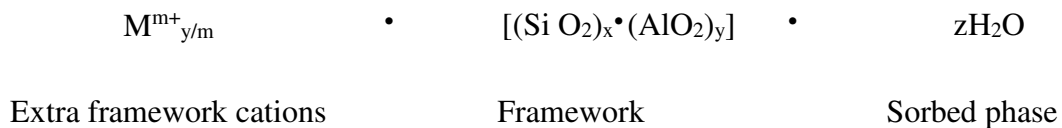
General information about zeolites

The discovery of zeolites dates to 1756 when the Swedish mineralogist Axel Fredrik Cronstedt observed the mineral stilbite emitting steam when being rapidly heated. For this reason the term zeolite was coined, which is derived from the two Greek words zeo, to boil, and lithos, stone, and thus can be translated as boiling stone.⁵

Zeolites are solids with intricate structures that possess channels and cages large enough to contain extra-framework cations and to permit the uptake and desorption of molecules varying from hydrogen to complex organics up to 1 nm in size. Their crystalline structure directly

controls their properties and consequently their performance in applications such as ion exchange, separation, and catalysis, and is therefore of great interest to academics and technologists alike.⁶

Strictly defined, zeolites are aluminosilicates with tetrahedrally connected framework structures based on corner-sharing TO₄ (basic building unit or BBU, where T besides Si and Al, can be Ge, Ti, B, Ga, P, etc.) tetrahedral with O atoms connecting neighboring tetrahedra. For a pure siliceous structure, combination of TO₄ (T = Si) units leads to formation of an uncharged solid. The aliovalent (Al³⁺ ↔ Si⁴⁺) substitution imparts an overall negative charge to the framework, and requires the presence of extra framework cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral.⁶⁻⁹ These charge-balancing cations are occupying the micropore space and because they are bonded to the lattice by Coulombic forces, different cations can exchange them. These compensating cations are introduced primarily during the synthesis of the zeolites and can be either inorganic, typically alkali metal ions, or organic such as quaternary ammonium ions.¹⁰ The zeolite composition can be best described as having three components:



where M is a cation with the charge m, (x + y) is the number of tetrahedra per crystallographic unit cell and x/y is the so-called framework silicon/aluminum ratio n_{Si} /n_{Al} (or simply Si/Al). The extra framework cations are ion exchangeable and give rise to the rich ion-exchange chemistry of these materials. Typically, in as-synthesized zeolites, water and organic non-framework cations present during synthesis occupies the internal voids of the material and can be removed by thermal treatment/oxidation, making the intercrystallite space available.^{11,12}

Typically, Al-O and Si-O bond distances are 1.73 and 1.61 Å, respectively, with OTO angles (T is the tetrahedral cation) close to the tetrahedral angle, 109.4°. There is more variation in the

Si $\hat{\text{O}}$ Si bond angles between tetrahedra, where the average angle is 154° with a range of 135-180° and a mode of 148°.8 Variation in T $\hat{\text{O}}$ T angles enables a wide diversity of frameworks to exist.¹³

The amount of Al within the framework can vary over a wide range, with Si/Al = 1 to ∞ . Löwenstein's rule precludes that two neighboring tetrahedra containing aluminum on tetrahedral positions, i.e. Al–O–Al linkages, are forbidden due to electrostatic repulsions between the negative charges. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increases.^{12,14}

Zeolites are usually classified into three classes, namely

- zeolites with low Si/Al ratios (<5),
- zeolites with medium Si/Al ratios (5 to 10) and
- zeolites with high Si/Al ratios (> 10).¹⁵

One of the unique properties of zeolites are (i) their strictly uniform pore diameters and (ii) pore widths in the order of molecular dimensions. According to IUPAC classification, the materials can be sort as follows:

microporous: $2.0\text{ nm} \geq d_p$,

mesoporous: $2.0\text{ nm} < d_p \leq 50\text{nm}$ and

macroporous: $d_p \geq 50\text{nm}$

with d_p being the pore diameter.¹⁶ Zeolites exhibit the pore size below 2 nm and thus belong to the group of the microporous materials.⁶⁻⁹

The framework tetrahedra are considered as the primary building blocks, which can be organized in secondary building units (SBU), containing up to 16 T-atoms. The condition for considering a finite group of T-atoms as an SBU is that it is present in at least two different tetrahedral framework topologies. The SBUs include rings with different numbers of tetrahedral cations (three-rings, four-rings, etc.), double four-rings, D4Rs, (which contain two

rings of four tetrahedral cations), D6Rs. These SBU are stacked together forming cages or channels which will finally build up the three-dimensional (3D) structure, characteristic of a given zeolite. The major part of this work has been performed on LTL-type zeolite; its SBUs are presented in Figure 1.^{5,6}

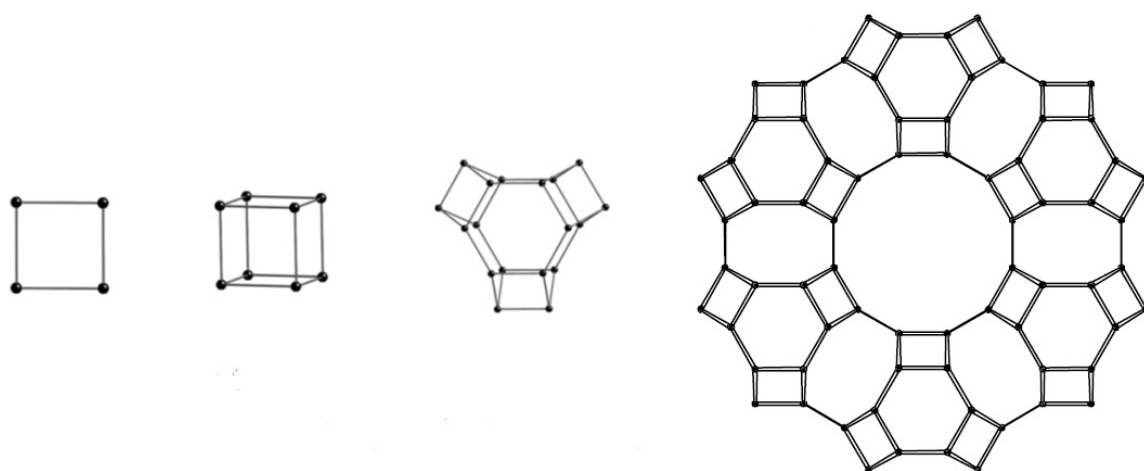


Figure 1 Schematic representation of building units (SBU): 4MR, D4R, and cancrinite cage in LTL-type zeolite

Pore openings are characterized by the size of the ring that defines the pore. An 8-ring is considered to be a small pore opening, a 10-ring a medium one, and a 12-ring a large one, with free diameters or effective pore widths (calculated using an oxygen radius of 1.35 Å) of ~4.1, 5.5, and 7.4 Å, respectively.⁸ The pores will belong to a channel system, which can be mono- (1D), di-dimensional (2D), or tri-dimensional, and that can be straight, sinusoidal, or follow a zigzag pattern. The channel system can be independent, or it can be interconnected with a second channel system.^{5,13}

Following the rules of an IUPAC Commission on Zeolite Nomenclature in 1979, three capital letters have been used throughout to designate the zeolite structures. The codes are generally derived from the names of the type material, e.g., FAU from the mineral faujasite, LTA from Linde Type A, and MFI from ZSM-5 (Zeolite Socony Mobil - five). The most recent Atlas of Zeolite Framework Types lists about 225 framework structures. However, only a few of those structure-types are of commercial interest and produced synthetically so far, viz. AEL, AFY,

*BEA, CHA, EDI, FAU, FER, GIS, LTA, LTL, MER, MFI, MOR, MTT, MWW, TON, and RHO.^{8,17}

Basic principles of zeolite synthesis

In general, zeolite materials are synthesized under hydrothermal–solvothermal conditions (temperatures between 100°C and 200°C), and the reaction gel medium contains the framework atoms, solvents, templates or structure-directing agents (SDAs), and mineralizers.¹⁸

Water is generally used as a solvent in zeolite synthesis. The main characteristics of water are the non-toxicity, low cost, good thermal stability, and conductivity. Also, it helps to the mineralizing agent to dissolve the species needed for the crystallization, and can act as template in association with other templating species.⁷

The role of a mineralizer is to increase the solubility of the silicate or aluminosilicate species, among others, in the synthesis gel by means of dissolution and precipitation, allowing the formation of supersaturated solutions.⁷ The mineralizing agent acts as a catalyst in those processes, which is consumed during the dissolution of species, and recovered after the zeolite crystallization.

The OH⁻ is the most extensively used mineralizing agent in the synthesis of zeolites. The hydroxyl anion increases the solubility of silicon and aluminium sources, directing the formation of soluble silicate and aluminate anions [Si(OH)_{4-n}O_nⁿ⁻, Al(OH)₄⁻]. The fluoride anions can be also used as mineralizing agent to reduce the alkalinity of the synthesis gel, that helps increasing the stability of OSDA molecules and their degradation by Hoffman mechanism.¹⁹

An alkali-metal hydroxide (NaOH, KOH...) in the synthesis gel leads to the formation of aluminium-rich zeolites. Large amount of positive charges introduced in the final crystalline solid by extra-framework small inorganic cations (Na⁺, K⁺...) must be balanced by the presence of large number of aluminium atoms in the framework. In contrast, when an organic structure

directing agent (OSDA), such as an amine or a quaternary ammonium salt, is introduced in the synthesis gel, the Si/Al ratio increases. This happens because bulky organic molecules occupy the zeolite channels volume providing less positive charges in the final solid, and therefore, less aluminium atoms in the framework are required.¹³

Zeolites synthesized by using heteroatom substitution

Until the late seventies, the extra framework species, such as exchangeable cations, have been the primary focus of researchers. But the discovery of titanium silicalite-1 and its wide catalytic potential by Taramasso et al.²⁰ already had triggered interest in this area, since it was soon realized that some rather specific coordination chemistry of lattice titanium ions was responsible for the unique catalytic properties of this material.²¹

The introduction of some heteroatoms (except Si, Al, P) in the zeolite framework may generate special chemical and physical properties. Moreover, heteroatoms have a great influence on the formation of zeolites. With the low level of substitution new T atoms may not affect the formation of the zeolite structure, or at higher concentrations, tend to give rise to novel structures. For example, Ge, B, Ga, Zn, and Be favor the formation of some particular building units (e.g., 4-rings, 3-rings, R4D, D3R, spiro-5 units, etc.) due to their suitable T–O bond and T–O–T angles and to their different ionic radii compared to Si⁴⁺, that can stabilize these building units. The initial work of heteroatom substitution is focused on the synthesis of the analogues of known aluminophosphate or aluminosilicate zeolites but with different properties. In the past few years, by introducing heteroatoms in the synthesis, many novel zeolites with low-framework density, extra-large pores, and chiral pores have been synthesized.^{6,13,18}

Silicon will be considered as the principal or key element of the framework. The probability of isomorphous substitution $\text{Si}^{4+} \leftrightarrow \text{Me}^{n+}$ and the stability of the Me^{n+} in the tetrahedral oxygen surrounding can be estimated using the Pauling criterion (ρ). In the simplified version $\rho = r_c/r_o$, where r_c is the cation radius and r_o is the radius of the oxygen ion. In accordance with

the literature, the tetrahedral surrounding should be stable for cations at $0.414 > \rho > 0.225$. This group of cations includes only few cations (Table 1). However, many cations, such as Fe^{3+} , Ga^{3+} or B^{3+} , have been proven to participate in the isomorphous substitution, if the concentration of this cation is low.^{7,13,22–24}

Table 1 Critical values (ρ) and preferred coordination numbers for chosen cations (adapted from [26])

Critical values (ρ)	Coordination number	Cations with the expected coordination number
$0.225 > \rho > 0.147$	3	B^{3+}
$0.414 > \rho > 0.225$	4	Al^{3+} , As^{5+} , Be^{2+} , Cr^{6+} , Ge^{4+} , Mn^{7+} , P^{5+} , Se^{6+} , Si^{4+}
$0.732 > \rho > 0.414$	6	As^{3+} , Bi^{5+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Ga^{3+} , Hf^{4+} , In^{3+} , Mn^{2+} , Mn^{4+} , Sb^{5+} , Sn^{4+} , Ta^{5+} , Ti^{3+} , Ti^{4+} , V^{4+} , V^{5+} , Zn^{2+} , Zr^{4+}
$\rho > 0.732$	8	Bi^{3+} , Ce^{2+} , Ce^{3+} , Eu^{3+} , Nd^{3+} , Pb^{2+} , Sn^{2+} , Ti^{3+}

The isomorphous substitution of Si by other tetrahedrally coordinated heteroatoms such as B^{3+} ,²⁵ Ti^{4+} (TS-1),^{26–31} Ga^{3+} ,^{32–36} and Fe^{3+} ,^{37–41} and Sn^{4+} ^{42–48} in small amounts (up to 2–3 wt.%) gives rise to new materials with tunable acidity showing specific catalytic properties in oxidation and hydroxylation reactions related to the coordination state of the heteroatom.^{49,50}

Nanosized zeolites

The driving force for many physical and chemical processes is the difference in the local environment of atoms exposed to solid surfaces compared to atoms in the bulk. There are two approaches to increase the number of surface atoms in solids, namely, to decrease the size of dense particles or to create an open pore network within the bulk of the solid. Both approaches result in an increase in the specific surface area of materials. The way to combine the two approaches and to maximize the amount of exposed to the surface atoms is to prepare nanosized particles containing accessible and uniform nanopores.⁵¹ Hence, the zeolites with a size of a crystal in the range of 5–1000 nm have attracted considerable attention during the last two decades. The reduction in particle size from micrometers to the nanometer scale leads to

substantial changes in their properties and thus different performances even in traditional applications are expected. The scaling down of zeolite crystals from the micrometer to the nanometer scale leads to enhanced zeolite properties such as increased surface area and decreased diffusion path lengths. As the crystal size is decreased below 100 nm, the zeolite external surface area, which is negligible for micron-sized zeolites, increases drastically, resulting in zeolites with over 25% of the total surface area on the external surface. If active sites are incorporated onto the external surface, high surface reactivity results, leading to zeolites with improved catalytic properties. Another advantage of nanocrystalline zeolites is the shorter diffusion path length in comparison to micron-sized zeolites. The possibility to obtain stable colloidal suspensions of microporous particles followed by assembling to optically transparent thin films on different substrates by rapid techniques is also of great importance for their advanced applications. The improved properties of nanocrystalline zeolites for adsorption and intracrystalline diffusion give rise to their application in environmental catalysis, environmental remediation, decontamination, and drug delivery.^{52–55}

The outstanding properties of zeolites with reduced particle sizes are summarized in Figure 2.



Figure 2 Properties of nanosized zeolites (reprinted from [57])

Nevertheless, the considerable decrease of zeolite crystal sizes also poses some negative consequences. For instance, the framework composition is influenced by the crystallization under very mild synthesis conditions and the sole use of organic structure directing agents. Zeolite materials synthesized under such conditions often exhibit a larger number of framework defects. The substantial decrease of crystalline domains often causes the broadening of the X-ray diffraction peaks, which is more pronounced in the case of particles smaller than 20 nm. Much larger external surface area of nanosized zeolites can not only bring some benefits to the system but also can be disadvantageous, for instance in stereoselective reactions, thus decreasing zeolite selectivity. The short diffusion path through zeolite channels could also have both desired and undesired consequences. This improves the kinetics of the reaction and limits coke formation, but on the other hand zeolite selectivity is corrupted.^{54,56}

The different approaches have been explored to obtain nanosized zeolites, namely confined space,⁵⁷ microreactor,⁵⁸ microwave (MW)⁵⁹ and ultrasonic radiation synthesis.⁶⁰ However conventional hydrothermal crystallization is mostly used. Hydrogels are used as precursors, but the way of preparation is particular in order to: i) favor the nucleation over the growth and ii) limit the aggregation between the growing crystals.⁵⁴

The post-synthesis treatment of the nanosized zeolites differs from one of micron-sized crystals, since the aggregation among the particles should be avoided. The nonconverted reactants are usually removed by high-speed centrifugation followed by the redispersion of zeolite nanoparticles in distilled water. The procedure is repeated several times until the pH of the resultant suspension is between 7 and 9. At this pH value the negative charge of the zeolite crystals is high enough to ensure colloidal stability. Freeze drying limits the aggregation between the crystallites during the drying procedure.^{54,56}

The crystalline nature of the framework ensures the uniformity of the pore openings throughout the crystal giving rise to a wide range of host–guest chemistry applications such as adsorption

and separation,^{61–63} ion exchange,^{5,64} catalysis,^{65,66} and sensor fabrication⁶⁷ due to their specific chemical compositions and unique porous structures. However, the potential uses of nanosized zeolites are going much beyond traditional catalysis, sorption and ion exchanges processes. These materials are considered in a number of advanced applications, where namely bulk materials were used.^{51,52,54–56,68} Recent developments of synthesis procedures for nanosized zeolites and their arrangements in thin-to-thick films, membranes and hierarchical forms (Figure 3) have pushed them into new and advanced applications that have not been considered before, including sensors, optical layers, medicine, pharmaceutical industry, cosmetics and food.^{13,51,53,55,68–83}

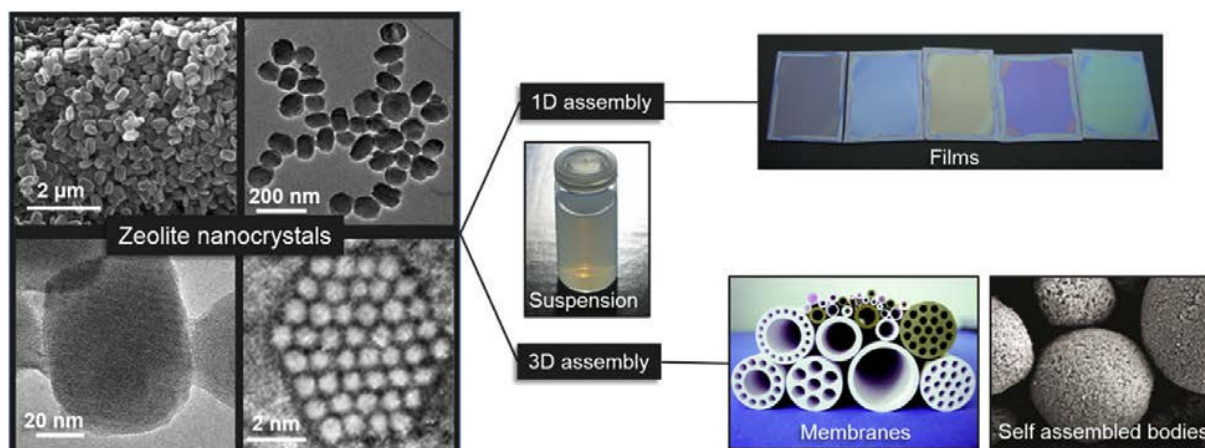


Figure 3 Nanosized zeolite crystals with a diverse morphology and size in colloidal suspensions, self-supported shapes, porous membranes, and optical quality films (reprinted from [56])

Metal nanoparticles

The importance of small metal clusters in catalysis and in many advanced applications elucidates from the significant physical changes that occur when reducing the size of a material down to a few nanometers; these systems often display unique nanochemical and nanophysical properties. As for many heterogeneous catalysts, controlling the nature, location and accessibility to catalytic sites are keys to ensuring optimal performance of metal-containing materials. The most active and selective catalysts, as well as novel optical and electronic materials, require precise nanoparticle size, geometry, dimensionality and easy accessibility by

reactants. Those criteria can be fulfilled during the formation of metal nanoclusters in confined matrices such as polymers, micro- and mesoporous materials.^{68,84–93}

Nanoparticles prepared from earth-abundant and inexpensive metals have attracted considerable attention because they are a viable alternative to the rare and expensive noble-metal catalysts used in many conventional commercial chemical processes.⁹⁴ These metal NPs often exhibit activity different from that of the corresponding bulk materials because of their different sizes and shapes, which give rise to distinctive quantum properties. In this context, Cu NPs are particularly attractive because of its high natural abundance and low cost and robust multiple ways of preparing Cu-based nanomaterials.^{95–98} Despite the strong background on the applications of bulk Cu in various fields (e.g., optics, electronics, etc.), the use of Cu NPs is restricted by instability under atmospheric conditions, which makes it prone to oxidation. Many efforts to develop the methods and supporting materials that increase the stability of Cu NPs by altering their sensitivity to oxygen, water, and other chemical entities has encouraged the exploration of alternative host for Cu NPs.⁴ Synthesis of copper nanoparticles

Numerous methods currently have been developed to produce copper nanoparticles.^{4,97,99}

Ultrasonic frequencies between 20 kHz and 15 MHz can be used to synthesize various nanostructures. Sonication promotes chemical reactions via acoustic cavitation, in which minute bubbles are formed and collapse to generate very high local temperatures and pressures. Sonochemical techniques make it possible to prepare nanomaterials under ambient conditions without the need for high temperatures, high pressures, or extended reaction times.^{100–103}

Microwave-assisted methods are widely used in organic synthesis due to their efficiency. In recent years, this method has also been used for preparing nanocrystals with high quality and narrow size distribution. Microwave irradiation can provide rapid and homogeneous heating, which is favorable for the synthesis of uniform and monodisperse nanoparticles.¹⁰⁴

Radiolytic reduction methods is a promising technique to synthesize various metal nanoparticles due to the simplicity, reproducibility, ambient conditions, and no additional chemical contamination during the process. In a radiolytic reduction method, solvated electrons, e_{aq}^- are firstly created by exposing aqueous solution to γ -rays. The solvated electrons then reduce metal ions to metallic clusters. With this method, the size of metal nanoparticles can be controlled by changing the stabilizer, radiation sources, concentration of precursors, etc.^{105,106}

A microemulsion is a type of thermodynamically and kinetically stable dispersion containing two immiscible liquids phases, e.g. oil and water. A microemulsion, with either water dispersed in oil or oil dispersed in water, provides a special liquid core-shell structure. The dimensions of the liquid cores are at the nanoscale level and thus can be used as chemical nanoreactors. Homogeneous metal nanoclusters could be formed and restricted inside the liquid core, and the particle size can be easily tuned by adjusting the liquid core dimensions of microemulsions.^{107,108}

Electrochemical synthesis has attracted considerable attention in nanomaterial fabrication mainly due to its low cost, low-temperature operation, high product purity, simplicity, and environmental friendliness. In electrochemical syntheses of Cu NPs, a steady current flow is applied through an electrolytic cell containing an aqueous solution of a Cu salt such as $CuSO_4$. This causes the electron transfer from the anode to the cathode, where the Cu ions are reduced to Cu atoms that subsequently agglomerate to form Cu NPs. In addition, it is also possible to obtain Cu NPs with specific morphologies by performing electrochemical synthesis in the presence of templates.^{109–111}

“Chemical treatment” stays for the methods in which Cu precursors are treated with external reagents that lead to copper reduction. Among all methods listed above, chemical reduction is the most favorable, because of the vast availability of reducing and capping agents, different

synthetic environments, and simpler laboratory techniques. It gives particles with various properties (size, morphology, stability) by tailoring the conditions of the reduction process, the nature of reducing agent, pH of reaction media and temperature, the molar ratio of the capping agent with the precursor salt and the ratio of reducing agent with the precursor salt.^{112–115} Reducing agents used for this purpose often include sodium borohydride, hydrazine, 1,2-hexadecane-diol, glucose, ascorbic acid, CO, or more recently introduced borane compounds.⁴

Supported copper nanoparticles

In most chemical reduction methods for synthesis of metal nanoparticles, protecting ligands are usually needed.⁹⁶ That is why special attention should be given to the materials used to support Cu NPs. The choice of support largely depends on the ease of its synthesis, its compatibility with different substrates/reagents, and, most importantly, the properties it poses on the resulting supported nanomaterials. Therefore, by choosing an appropriate support, it is possible to modify the properties of the NPs to suit specific applications.⁴

Several supports have been extensively used and have been summarized in several reviews.^{4,116} For example, activated carbon and diamond NPs have been used as supports for catalytically active metals. A variety of metal oxides have been examined as supporting materials for Cu-based NPs. Ceria is an important support material for various catalysts due to its oxygen content, which is particularly high at its surfaces. Another important support materials that has been widely used as a support for NPs are alumina, MgO, titania and zirconia.

Silica- and silicon-supported nanomaterials have been used extensively in fields ranging from catalysis to adsorption and optics, among others. Silica supports contain surface silanols that simplifies NPs binding, while silicon has unique electronic and optical properties allowing the preparation of sophisticated multifunctional hybrid materials. Due to its controllable pore size and shape as well as its large surface area mesoporous silica represents an ideal supporting material for many types of NPs.

Zeolite have been broadly used as a support for metal NPs for different applications including catalysis and adsorption, because of their unique porous morphology. Usually, the final nanomaterials are prepared by copper ion exchange of the parent zeolite followed by the reduction of the copper cations occluded in the zeolite channels. The steric hindrance imposed by the zeolite cages controls the size of the resulting Cu nanoclusters, and the limited pore diameter increases the catalytic selectivity.^{88,117} The variety of zeolite structures permits the creation of diverse materials of reduced dimensionality. Copper containing zeolites are of great interest due to the low cost of copper and its excellent catalytic activity in a wide range of reactions, including selective catalytic reduction of NO, synthesis and decomposition of methanol and higher alcohols, etc. The performance of these materials in the above applications depends on the location, coordination state, reactivity and mobility of copper species in the zeolite frameworks.^{118–126} Some examples of different metal nanoparticles stabilized in the zeolites are summarized in the Table 2.^{86,87,92,127–144}

Nanosized zeolites are alternative hosts (matrix) for stabilization of metal NPs. The combination of the transport properties within the porous framework structures with the chemical reactivity of the metal clusters is a promising pathway to the development of advanced materials which are interesting for numerous applications in nanoscale devices, selective chemical sensing, catalysis, nanoelectronics, data storage, molecular imaging, biosensing, nanomedicine ect.^{91,145–152}

Table 2 The examples of metal nanoparticles supported on zeolites

Literature source	Zeolite	Me	Me incorporation	Reduction method	Comments
[127]	BEA	Ag	Ion exchange with AgClO ₄	Pulse radiolysis	
[128]	FAU	Ag	Ion exchange with AgNO ₃	UV irradiation	0.75 – 1.12 nm
[129]	EMT	Ag	Ion exchange with AgClO ₄	Microwave reduction (120 °C, 10 min, 1000 W) in the presence of a triethylamine N(C ₂ H ₅) ₃	0.5 – 0.7 nm
[130]	LTL	Ag	Ion exchange with AgNO ₃	In hydrogen flow at 500 °C; Under oxidative conditions	20 – 32 nm 3 – 4 nm
[92]	Zeolite Y	Ag	Ion exchange with AgNO ₃	Resorcinol in aqueous solution all at room temperature in dark	2.45 nm after 120 min
[86]	MOR	Ag, Cu	Ion exchange with AgNO ₃ , Cu(NO ₃) ₂	In hydrogen flow, 20–450 °C, 240 min	
[131]	Zeolite Y	Cu	Ion exchange	Hydrazine hydrate at 60 °C for 180 min	8 nm
[87]	LTL	Cu	Ion exchange with Cu(NO ₃) ₂	Hydrazine hydrate at RT for 280 min	1 – 2.2 nm
[132]	Mordenites, erionite and clinoptilolite	Cu	Ion exchange with Cu(NO ₃) ₂	In hydrogen flow under fixed temperatures 150, 250, 350 and 450 °C	2 – 10 nm
[133]	Zeolite Y	Cu	Caking with CuCl for 24 h at 420 °C under high vacuum	In hydrogen flow at 460 and 600 °C	Aggregates of 5 nm
[134]	GIS	Cu	Ion exchange with Cu(NO ₃) ₂	γ radiolysis	0.23 – 1.26 nm
[135]	Zeolite Y	Fe, Cu, Mn	Ion exchange with FeCl ₃ ·6H ₂ O, CuCl ₂ ·2H ₂ O, and MnCl ₂ ·4H ₂ O	Sodium borohydride in aqueous solution at 20 °C	Metallic and bimetallic nanoparticles

[136]	Silicalite-1 ZSM-5	Au	Immobilization of as-prepared Au NPs in amorphous silica matrix		1 – 3 nm
[137]	LTA	Au, Pd, Pt	Hydrothermal assembly of LTA crystals around cationic precursors ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$, H_2PtCl_6) stabilized by protecting mercaptosilane ligands	In hydrogen flow at 350 °C	1.5 – 3 nm AuPd, AuPt, and PdPt bimetallic clusters
[138]	Zeolite Beta	Pt	Ion exchange with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	γ radiolysis	0.23 – 1.26 nm
[139]	FAU-LTA hierarchical porous composite	Pt	Ion-exchanged with $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$	Reduction in hydrogen atmosphere	1 – 5 nm
[140]	BEA	Pt	Ion-exchange with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$	Plasma treatment	2 nm
[141]	CHA	Pt	Hydrothermal assembly of CHA crystals around cationic precursor ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$)	In hydrogen flow at 400 °C	1 nm
[142]	Natural zeolite (<10 μm powder, 0.6 K_2O : 4.0 Na_2O : 1 Al_2O_3 : 2.0 SiO_2 : H_2O , Sigma Aldrich)	Pd	Ion-exchange with palladium acetylacetonate $\text{Pd}(\text{acac})_2$	Hydrazine hydrate in aqueous solution	
[143]	Zeolite Y	Os	Ion exchange with $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$	Sodium borohydride in aqueous solution at room temperature	3 – 4 nm
[144]	Silicalite-1	Ni	Incipient wetness impregnation with $\text{Ni}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$	In hydrogen flow at 750 °C	10 nm

Growth mechanism of copper nanoparticles

It has been widely accepted that the process of the nucleation and growth of nanoparticles can be described through the LaMer burst nucleation followed by Ostwald ripening. The process was initially modeled by Reiss using the model developed by Lifshitz–Slyozov–Wagner (LSW theory). However, thanks to in- and ex-situ UV-vis spectroscopy, Watzky and Finke formulated an approach of constant slow nucleation followed by autocatalytic growth.¹⁵³

a. LaMer Mechanism

Victor K. LaMer proposed the mechanism^{154,155} which involves the separation of the nucleation and growth into two stages. The process of nucleation and growth by LaMer mechanism can be divided into three stages: (i) A rapid increase in the concentration of free monomers in solution, (ii) “burst-nucleation” of the monomer which significantly reduces the concentration of free monomers in solution. Later, there is almost no nucleation occurring due to the low concentration of monomers after this point; (iii) the growth occurs under the control of the diffusion of the monomers through the solution.

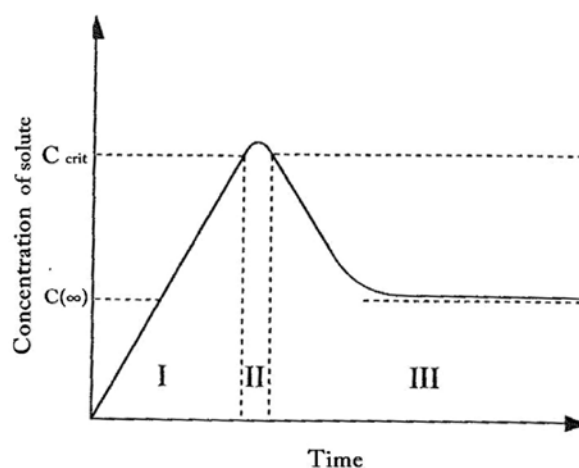


Figure 4 Schematic representation of LaMer mechanism (reprinted from [126])

b. Ostwald Ripening and Digestive Ripening

Colloid particles become increasingly unstable with decreasing of the particle size due to the relative increase in energy surface. The Gibbs – Thomson equation describes the change in the

particles solubility with the change of the size in terms of the solubility concentration, $C(r)$, of a particle with radius r .¹⁵⁶

$$C(r) = C^{\circ} \exp\left(\frac{2\gamma V_m}{rRT}\right),$$

where C° is the solubility of an atom taken from an infinite flat surface, V_m is the molar volume of the particle, γ is the surface energy, R is the gas constant, and T is the temperature. This size-dependent instability leads to Ostwald ripening, which is the transfer of atoms over time from smaller, less stable particles to larger ones. Digestive ripening is effectively the inverse of Ostwald ripening, where smaller particles grow at expense of the larger ones.^{153,156}

c. The Finke – Watzky two step mechanism

The Finke-Watzky two step mechanism can be described as nucleation and growth happening simultaneously. The first stage is a slow continuous nucleation (I) $A \rightarrow B$, and the second is the autocatalytic surface growth which is not diffusion controlled (II) $A + B \rightarrow 2B$.¹⁵⁷

d. Coalescence and Orientated Attachment

Coalescence and orientated attachment are very similar. The difference is in the orientation of the crystal lattice at the grain boundary. There is no particular preference for the attachment when the coalescence takes place, whereas for the orientated attachment, there is a common crystallographic alignment of the attachment to occur, allowing the continuous crystallographic planes.¹⁵³

Goals

Literature overview shows the importance and tremendous interests in the preparation of metal-containing nanosized zeolites, driven by their numerous promising applications, including catalysis, photo-catalysis, gas separation, chemical sensing, etc. These materials are particularly useful for addressing environmental issues and energy saving.

Hence, the main goal of this study is to develop synthesis and characterization strategies for the preparation of copper and, also, silver-containing nanozeolites in the form of powders,

suspensions, and films, and to explore their abilities for photo-catalytical and chemical sensing applications.

The first task was to study the kinetics of copper nanoparticles within the cavities of nanosized LTL zeolite crystals prepared in the form of the water suspension.

Due to complexity of the system copper nanoparticles – zeolite matrix special attention has been paid to the characterization and quantification of all copper species, that are present in the host and can influence the activity of the new material in various applications.

The third objective is to compare the nature of copper species formed in the nanosized zeolites using two approaches: (i) direct incorporation of Cu via one pot synthesis, and (ii) post synthesis incorporation. Special attention is paid to the environment and location of the copper species within the zeolite crystals.

The forth task is to reveal the potential and the current limitations of fabrication of chemical sensors based on zeolite thin films. Spin-coating approach for deposition of metal-containing nanosized zeolites for was applied with the ultimate goal of preparation of low cost detectors for low concentrations on harmful gases, such as CO.

The final objective is to investigate the host-guest photoreactivity in silver-containing zeolites. In order to address the ultrafast processes involved in the plasmonic behavior of Ag-zeolite host-guest systems, a novel route consisting of transient absorption measurements on transparent metal-containing zeolite thin films was applied.

References

- 1 A. Steinfeld, C.- Zurich and R. Palumbo, *Encycl. Phys. Sci. Technol.*, 2001, **15**, 237–256.
- 2 S. Licht, *Chem. Commun. (Camb)*., 2005, **2005**, 4635–4646.
- 3 R. R. Conry, *Encycl. Inorg. Chem.*, 2006, 1–19.
- 4 M. B. Gawande, A. Goswami, F.-X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril and R. S. Varma, *Chem. Rev.*, 2016, **116**, 3722–3811.
- 5 C. Martínez and A. Corma, *Compr. Inorg. Chem. II*, 2013, 103–131.
- 6 J. Cejka, A. Corma and S. Zones, Eds., *Zeolites and Catalysis. Synthesis, Reactions and Applications*, Wiley-VCH Verlag GmbH & Co. KGaA., 2010.
- 7 J. Weitkamp and L. Puppe, Eds., *Catalysis and Zeolites. Fundamentals and Applications*, Springer-Verlag Berlin Heidelberg, 1st editio., 1999.
- 8 J. Cejka, H. van Bekkum, A. Corma and F. Schueth, *Introduction to Zeolite Science and Practice- 3rd Revised Edition*, Elsevier, 3rd editio., 2007.
- 9 P. Eliášová, M. Opanasenko, P. S. Wheatley, M. Shamzhy, M. Mazur, P. Nachtigall, W. J. Roth, R. E. Morris and J. Čejka, *Chem. Soc. Rev.*, 2015.
- 10 A. Primo and H. Garcia, *Chem. Soc. Rev.*, 2014, **43**, 7548–7561.
- 11 S. M. Auerbach, K. A. Carrado and P. K. Dutta, *Handbook of zeolite science and technology*, CRC Press, 2004, vol. 2004.
- 12 J. Weitkamp, *Solid State Ionics*, 2000, **131**, 175–188.
- 13 C. Martinez and J. Perez-Pariente, Eds., *Structural Chemistry and Properties of Zeolites*, 1st edn., 2011.
- 14 P. Payra and P. K. Dutta, in *Handbook of Zeolite Science and Technology*, 2003.
- 15 *Catalysis and Zeolites*, 1999.
- 16 D. H. Everett, *Pure Appl. Chem.*, 1973.
- 17 C. Baerlocher, L. McCusker and D. Olson, *Atlas of zeolite framework types*, 2007, vol. 12.
- 18 J. Li, A. Corma and J. Yu, *Chem. Soc. Rev.*, 2015.
- 19 C. S. Cundy and P. a Cox, 2003, **103**, 663–702.
- 20 G. Perego, G. Bellusi, C. Corno, M. Taramasso, F. Buonomo and A. Esposito, *Stud. Surf. Sci. Catal.*, 1986, **28**, 129–136.
- 21 G. Bellussi and M. S. Rigutto, in *Advanced Zeolite Science and Applications*, eds. J.C. Jansen, M. Stocker, H. G. Karge and J. Weitkamp, Elsevier B.V, 1994, vol. 85, pp. 177–213.
- 22 K. G. Ione, L. A. Vostrikova and V. M. Mastikhin, *J. Mol. Catal.*, 1985, **31**, 355–370.
- 23 K. G. Ione and L. A. Vostrikova, *Russ. Chem. Rev.*, 1987, **56**, 393–427.
- 24 B. Sulikowski, *Heterog. Chem. Rev.*, 1996, **3**, 203–268.
- 25 G. Coudurier, A. Auroux, J. C. Vedrine, R. D. Farlee, L. Abrams and R. D. Shannon, *J. Catal.*, 1987, **108**, 1–14.
- 26 S. Bordiga, A. Damin, F. Bonino, G. Ricchiardi, C. Lamberti and A. Zecchina, *Angew. Chemie - Int. Ed.*, 2002, **41**, 4734–4737.
- 27 G. Ricchiardi, A. Damin, S. Bordiga, C. Lamberti, G. Spanò, F. Rivetti and A. Zecchina, *J. Am. Chem. Soc.*, 2001, **123**, 11409–11419.
- 28 R. Millini, E. Previde Massara, G. Perego and G. Bellussi, *J. Catal.*, 1992, **137**, 497–503.
- 29 G. Tozzola, M. a. Mantegazza, G. Ranghino, G. Petrini, S. Bordiga, G. Ricchiardi, C. Lamberti, R. Zulian and A. Zecchina, *J. Catal.*, 1998, **179**, 64–71.
- 30 C. Lamberti, S. Bordiga, A. Zecchina, A. Carati, N. N. Fitch, G. Artioli, G. Petrini, M. Salvalaggio and G. L. L. Marra, *J. Catal.*, 1999, **183**, 222–231.

- 31 S. Bordiga, F. Boscherini, S. Coluccia, F. Genonic, C. Lamberti, G. Leofanti, L. Marchese, G. Petrini, G. Vlaic and A. Zecchina, *Catal. Letters*, 1994, **26**, 195–208.
- 32 R. Fricke, H. Kosslick, G. Lischke and M. Richter, *Chem. Rev.*, 2000, **100**, 2303–2405.
- 33 C. Lamberti, G. T. Palomino, S. Bordiga, A. Zecchina and G. Span, *Science (80-.)*, 1999, **63**, 213–216.
- 34 C. Otero Areán, G. Turnes Palomino, F. Geobaldo and a. Zecchina, *J. Phys. Chem.*, 1996, **100**, 6678–6690.
- 35 X. Liu and J. Klinowski, *J. Phys. Chem.*, 1992, **311**, 3403–3408.
- 36 C. R. Bayense, A. P. M. Kentgens, J. W. De Haan, L. J. M. Van de Ven and J. H. C. Van Hooff, *J. Phys. Chem.*, 1992, **96**, 775–782.
- 37 G. Berlier, G. Spoto, S. Bordiga, G. Ricchiardi, P. Fisicaro, A. Zecchina, I. Rossetti, E. Selli, L. Forni, E. Giamello and C. Lamberti, *J. Catal.*, 2002, **208**, 64–82.
- 38 S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola and G. Vlaic, *J. Catal.*, 1996, **158**, 486–501.
- 39 A. Zecchina, F. Geobaldo, C. Lamberti, S. Bordiga, G. Turnes Palomino and C. Otero Arean, *Catal. Letters*, 1996, **42**, 25–33.
- 40 R. Szostak and T. L. Thomas, *J. Catal.*, 1986, **100**, 555–557.
- 41 R. Kumar and P. Ratnasamy, *J. Catal.*, 1990, **121**, 89–98.
- 42 S. N. Talapaneni, J. Grand, S. Thomas, H. A. Ahmad and S. Mintova, *Mater. Des.*, 2016, **99**, 574–580.
- 43 S. Tolborg, A. Katerinopoulou, D. D. Falcone, I. Sádaba, C. M. Osmundsen, R. J. Davis, E. Taarning, P. Fristrup and M. S. Holm, *J. Mater. Chem. A*, 2014, **2**, 20252–20262.
- 44 T. Iida, A. Takagaki, S. Kohara, T. Okubo and T. Wakihara, *ChemNanoMat*, 2015, **1**, 155–158.
- 45 H. Y. Luo, L. Bui, W. R. Gunther, E. Min and Y. Román-Leshkov, *ACS Catal.*, 2012, **2**, 2695–2699.
- 46 W. R. Gunther, Y. Wang, Y. Ji, V. K. Michaelis, S. T. Hunt, R. G. Griffin and Y. Román-Leshkov, *Nat. Commun.*, 2012, **3**, 1109.
- 47 S. Roy, K. Bakhmutsky, E. Mahmoud, R. F. Lobo and R. J. Gorte, *ACS Catal.*, 2013, **3**, 573–580.
- 48 A. Corma, L. T. Nemeth, M. Renz and S. Valencia, *Nature*, 2001, **412**, 423–425.
- 49 R. Szostak, *Molecular Sieves. Principles of Synthesis and Identification*, 1988.
- 50 R. Aiello, J. B. Nagy, G. Giordano, A. Katovic and F. Testa, *Comptes Rendus Chim.*, 2005, **8**, 321–329.
- 51 V. Valtchev and L. Tosheva, *Chem. Rev.*, 2013, **113**, 6734–6760.
- 52 S. Mintova and E.-P. Ng, in *Comprehensive Inorganic Chemistry II: From Elements to Applications*, 2013, vol. 5, pp. 285–302.
- 53 S. C. Larsen, *J. Phys. Chem. C*, 2007, **111**, 18464–18474.
- 54 S. Mintova, J. Grand and V. Valtchev, *Comptes Rendus Chim.*, 2016, **19**, 183–191.
- 55 M. Zaarour, B. Dong, I. Naydenova, R. Retoux and S. Mintova, *Microporous Mesoporous Mater.*, 2014, **189**, 11–21.
- 56 S. Mintova, M. Jaber and V. Valtchev, *Chem. Soc. Rev.*, 2015, **44**, 7207–7233.
- 57 C. Madsen, C. Madsen and C. J. H. Jacobsen, *Chem. Commun.*, 1999, 673–674.
- 58 Y. Pan, M. Ju, J. Yao, L. Zhang and N. Xu, *Chem. Commun. (Camb.)*, 2009, 7233–5.
- 59 C. Jo, J. Jung, H. S. Shin, J. Kim and R. Ryoo, *Angew. Chemie - Int. Ed.*, 2013, **52**, 10014–10017.
- 60 S. Askari, S. Miar Alipour, R. Halladj and M. H. Davood Abadi Farahani, *J. Porous Mater.*, 2012, **20**, 285–302.
- 61 J. Gascon, F. Kapteijn, B. Zornoza, V. Sebastián, C. Casado and J. Coronas, *Chem.*

- Mater.*, 2012, **24**, 2829–2844.
- 62 N. Kosinov, V. G. P. Sripathi and E. J. M. Hensen, *Microporous Mesoporous Mater.*, 2014, **194**, 24–30.
 - 63 N. Kosinov, C. Auffret, V. G. P. Sripathi, C. Gücüyener, J. Gascon, F. Kapteijn and E. J. M. Hensen, *Microporous Mesoporous Mater.*, 2014, **197**, 268–277.
 - 64 D. W. Breck, *J. Chem. Educ.*, 1964, **41**, 678–689.
 - 65 K. Li, J. Valla and J. Garcia-Martinez, *ChemCatChem*, 2014, **6**, 46–66.
 - 66 I. Fechete, Y. Wang and J. C. V??drine, *Catal. Today*, 2012, **189**, 2–27.
 - 67 R. Moos, *Sensors*, 2010, **10**, 6773–6787.
 - 68 T. Bein and S. Mintova, *Zeolites and Ordered Mesoporous Materials: Progress and Prospects*, Elsevier, 2005, vol. 157.
 - 69 S. Mintova and T. Bein, *Microporous Mesoporous Mater.*, 2001, **50**, 159–166.
 - 70 Y. Zheng, X. Li and P. K. Dutta, *Sensors*, 2012, **12**, 5170–5194.
 - 71 T. Baimpos, L. Gora, V. Nikolakis and D. Kouzoudis, *Sensors Actuators A Phys.*, 2012, **186**, 21–31.
 - 72 D. J. Wales, J. Grand, V. P. Ting, R. D. Burke, K. J. Edler, C. R. Bowen, S. Mintova and A. D. Burrows, *Chem. Soc. Rev.*, 2015.
 - 73 M. Vilaseca, J. Coronas, A. Cirera, A. Cornet, J. R. Morante and J. Santamaría, *Catal. Today*, 2003, **82**, 179–185.
 - 74 K. Sahner, G. Hagen, D. Schönauer, S. Reiß and R. Moos, *Solid State Ionics*, 2008, **179**, 2416–2423.
 - 75 C. M. Lew, R. Cai and Y. Yan, *Acc. Chem. Res.*, 2010, **43**, 210–219.
 - 76 M. Moothanchery, I. Naydenova, S. Mintova and V. Toal, *Opt. Express*, 2011, **19**, 25786–25791.
 - 77 US pat., 20090130154 A1, 2009.
 - 78 S. E. Lehman and S. C. Larsen, *Environ. Sci. Nano*, 2014, **1**, 200–213.
 - 79 N. Tirtaatmadja, G. Mortimer, E.-P. Ng, H. A. Ahmad, S. Mintova, V. Serpooshan, R. F. Minchin and M. Mahmoudi, *J. Iran. Chem. Soc.*, 2014, **12**, 317–323.
 - 80 A. Petushkov, J. Intra, J. B. Graham, S. C. Larsen and A. K. Salem, *Chem. Res. Toxicol.*, 2009, **22**, 1359–1368.
 - 81 J. A. Litch and R. A. Bishop, *Wilderness Environ. Med.*, 2000, **11**, 189–191.
 - 82 T. Babeva, H. Awala, M. Vasileva, J. El Fallah, K. Lazarova, S. Thomas and S. Mintova, *Dalton Trans.*, 2014, **43**, 8868–8876.
 - 83 E. Leite, T. Babeva, E. P. Ng, V. Toal, S. Mintova and I. Naydenova, *J. Phys. Chem. C*, 2010, **114**, 16767–16775.
 - 84 A. Seidel, J. Loos and B. Boddenberg, *J. Mater. Chem.*, 1999, 2495–2498.
 - 85 V. Gurin and V. Petranovskii, *Stud. Surf. Sci. Catal.*, 2004, **154**, 1661–1669.
 - 86 V. S. Gurin, V. P. Petranovskii, M. -a. Hernandez, N. E. Bogdanchikova and a. a. Alexeenko, *Mater. Sci. Eng. A*, 2005, **391**, 71–76.
 - 87 A. Kharchenko, O. I. Lebedev, V. Zholobenko, V. de Waele and S. Mintova, *J. Phys. Chem. C*, 2016, acs.jpcc.6b08045.
 - 88 K.-L. Wong, A. Souici, V. De Waele, M. Mostafavi, T. H. Metzger and S. Mintova, *Langmuir*, 2010, **26**, 4459–64.
 - 89 M. Zahmakiran, F. Durap and S. Özkar, *Int. J. Hydrogen Energy*, 2010, **35**, 187–197.
 - 90 V. De Waele, J. Kecht, Z. Tahri, M. Mostafavi, T. Bein and S. Mintova, *Sensors Actuators B Chem.*, 2007, **126**, 338–343.
 - 91 J. Kecht, Z. Tahri, V. De Waele, M. Mostafavi, S. Mintova and T. Bein, *Chem. Mater.*, 2006, **18**, 3373–3380.
 - 92 M. Severance and P. K. Dutta, *J. Phys. Chem. C*, 2014, **118**, 28580–28591.
 - 93 D. Farrusseng and A. Tuel, *New J. Chem.*, 2016.

- 94 F. Zaera, *Chem. Soc. Rev.*, 2013, **2**, 2746–2762.
- 95 G. Evano, N. Blanchard and M. Toumi, *Chem. Rev.*, 2008, **108**, 3054–3131.
- 96 Y. Lu and W. Chen, *Chem. Soc. Rev.*, 2012, **41**, 3594–623.
- 97 N. Cioffi, N. Ditaranto, L. Torsi and L. Sabbatini, *Approaches to synthesis and characterization of spherical and anisotropic copper nanomaterials*, 2009.
- 98 P. Christian, F. Von Der Kammer, M. Baalousha and T. Hofmann, *Ecotoxicology*, 2008, **17**, 326–343.
- 99 Y. Xia and N. J. Halas, *MRS Bull.*, 2011, **30**, 338–348.
- 100 R. V. Kumar, Y. Mastai, Y. Diamant and a. Gedanken, *J. Mater. Chem.*, 2001, **11**, 1209–1213.
- 101 J. Moghimi-Rad, F. Zabihi, I. Hadi, S. Ebrahimi, T. D. Isfahani and J. Sabbaghzadeh, *J. Mater. Sci.*, 2010, **45**, 3804–3811.
- 102 M. Veerapandian, R. Subbiah, G. S. Lim, S. H. Park, K. Yun and M. H. Lee, *Langmuir*, 2011, **27**, 8934–8942.
- 103 B. K. Park, S. Jeong, D. Kim, J. Moon, S. Lim and J. S. Kim, *J. Colloid Interface Sci.*, 2007, **311**, 417–424.
- 104 M. Blosi, S. Albonetti, M. Dondi, C. Martelli and G. Baldi, *J. Nanoparticle Res.*, 2011, **13**, 127–138.
- 105 S. S. Jushi, S. F. Patil, V. Iyer and S. Mahumuni, *NanoStructured Mater.*, 1998, **10**, 1135–1144.
- 106 J. Ryu, H.-S. Kim and H. T. Hahn, *J. Electron. Mater.*, 2011, **40**, 42–50.
- 107 I. Lisiecki and M. P. Pileni, *J. Am. Chem. Soc.*, 1993, **115**, 3887–3896.
- 108 M. P. Pileni, B. W. Ninham, T. Gulik-Krzywicki, J. Tanori, I. Lisiecki and a Filankembo, *Adv. Mater.*, 1999, **11**, 1358–1362.
- 109 Y. G. Guo, J. S. Hu and L. J. Wan, *Adv. Mater.*, 2008, **20**, 2878–2887.
- 110 G.-R. Li, H. Xu, X.-F. Lu, J.-X. Feng, Y.-X. Tong and C.-Y. Su, *Nanoscale*, 2013, 1–35.
- 111 A. S. Arico, P. Bruce, B. Scrosati and J.-M. Arascon, *Nature*, 2005, **4**, 366–377.
- 112 T. M. D. Dang, T. T. T. Le, E. Fribourg-Blanc and M. C. Dang, *Adv. Nat. Sci. Nanosci. Nanotechnol.*, 2011, **2**, 15009.
- 113 D. Deng, Y. Jin, Y. Cheng, T. Qi and F. Xiao, 2013.
- 114 Y. Kobayashi, S. Ishida, K. Ihara, Y. Yasuda, T. Morita and S. Yamada, *Colloid Polym. Sci.*, 2009, **287**, 877–880.
- 115 S. Mallick, S. Sharma, M. Banerjee, S. S. Ghosh, A. Chattopadhyay and A. Paul, *ACS Appl. Mater. Interfaces*, 2012, **4**, 1313–1323.
- 116 J. E. Mondloch, E. Bayram and R. G. Finke, *J. Mol. Catal. A Chem.*, 2012, **355**, 1–38.
- 117 A. Souici, K.-L. Wong, V. De Waele, J. L. Marignier, T. H. Metzger, N. Keghouche, S. Mintova and M. Mostafavi, *J. Phys. Chem. C*, 2014, **118**, 6324–6334.
- 118 S. a. Anderson, S. Manthata and T. W. Root, *Appl. Catal. A Gen.*, 2005, **280**, 117–124.
- 119 W. X. Zhang, H. Yahiro, N. Mizuno, J. Izumi and M. Iwamoto, *Langmuir*, 1993, **9**, 2337–2343.
- 120 M. Iwamoto, *Stud. Surf. Sci. Catal.*, 1991, 327–334.
- 121 C. Torre-Abreu, C. Henriques, F. . Ribeiro, G. Delahay and M. . Ribeiro, *Catal. Today*, 1999, **54**, 407–418.
- 122 N. V. Beznis, B. M. Weckhuysen and J. H. Bitter, *Catal. Letters*, 2010, **138**, 14–22.
- 123 G. D. Pirngruber, *Ordered Porous Solids*, 2009, 749–771.
- 124 F. Márquez, a. E. Palomares, F. Rey and a. Corma, *J. Mater. Chem.*, 2001, **11**, 1675–1680.
- 125 S. Chassaing, A. Sani Souna Sido, A. Alix, M. Kumarraja, P. Pale and J. Sommer, *Chem. - A Eur. J.*, 2008, **14**, 6713–6721.

- 126 W. Zhang, J. Xie, W. Hou, Y. Liu, Y. Zhou and J. Wang, 2016.
- 127 Z. Tahri, F. Luchez, I. Yordanov, O. Poizat, A. Moissette, V. Valtchev, S. Mintova, M. Mostafavi and V. De Waele, *Res. Chem. Intermed.*, 2009, **35**, 379–388.
- 128 M. Zaarour, M. El Roz, B. Dong, R. Retoux, R. Aad, J. Cardin, C. Dufour, F. Goubilleau, J.-P. Gilson and S. Mintova, *Langmuir*, 2014, **30**, 6250–6.
- 129 B. Dong, R. Retoux, V. de Waele, S. G. Chiodo, T. Mineva, J. Cardin and S. Mintova, *Microporous Mesoporous Mater.*, 2017.
- 130 R. Bartolomeu, R. Bértolo, S. Casale, A. Fernandes, C. Henriques, P. Da Costa and F. Ribeiro, *Microporous Mesoporous Mater.*, 2013, **169**, 137–147.
- 131 T. Subramanian and K. Pitchumani, *Catal. Sci. Technol.*, 2012, **2**, 296.
- 132 A. N. Pestryakov, V. P. Petranovskii, A. Kryazhov, O. Ozhereliev, N. Pfänder and A. Knop-Gericke, *Chem. Phys. Lett.*, 2004, **385**, 173–176.
- 133 A. Seidel, J. Loos and B. Boddenberg, *J. Mater. Chem.*, 1999, **9**, 2495–2498.
- 134 L. Lakiss, J. Kecht, V. de Waele and S. Mintova, *Superlattices Microstruct.*, 2008, **44**, 617–625.
- 135 Y. Zeng, H. Walker and Q. Zhu, *J. Hazard. Mater.*, 2016, **324**, 605–616.
- 136 K. T. Højholt, A. B. Laursen, S. Kegnæs and C. H. Christensen, *Top. Catal.*, 2011, **54**, 1026–1033.
- 137 T. Otto, J. M. Ramallo-López, L. J. Giovanetti, F. G. Requejo, S. I. Zones and E. Iglesia, *J. Catal.*, 2016, **342**, 125–137.
- 138 I. Yordanov and R. Knoerr, *J. ...*, 2010, 20974–20982.
- 139 X. Zou, K.-L. Wong, S. Thomas, T. H. Metzger, V. Valtchev and S. Mintova, *Catal. Today*, 2011, **168**, 140–146.
- 140 M. Rivallan, I. Yordanov, S. Thomas, C. Lancelot, S. Mintova and F. Thibault-Starzyk, *ChemCatChem*, 2010, **2**, 1074–1078.
- 141 M. Moliner, J. E. Gabay, C. E. Klier, R. T. Carr, J. Guzman, G. L. Casty, P. Serna and A. Corma, *J. Am. Chem. Soc.*, 2016, **354**, jacs.6b10169.
- 142 J. Choi, S. Chan, G. Yip, H. Joo, H. Yang and F. K. Ko, *Water Res.*, 2016, **101**, 46–54.
- 143 M. Zahmakiran, S. Akbayrak, T. Kodaira and S. Ozkar, *Dalt. Trans.*, 2010, **39**, 7521–7527.
- 144 D. Laprune, C. Theodoridi, A. Tuel, D. Farrusseng and F. C. Meunier, *Appl. Catal. B Environ.*, 2017, **204**, 515–524.
- 145 X. Zou, J.-M. Goupil, S. Thomas, F. Zhang, G. Zhu, V. Valtchev and S. Mintova, *J. Phys. Chem. C*, 2012, **116**, 16593–16600.
- 146 Y. Lee, J.-R. Choi, K. J. Lee, N. E. Stott and D. Kim, *Nanotechnology*, 2008, **19**, 415604.
- 147 M. Kaya, M. Zahmakiran, S. Özkar and M. Volkan, *ACS Appl. Mater. Interfaces*, 2012, **4**, 3866–3873.
- 148 A. P. Ingle, N. Duran and M. Rai, *Appl. Microbiol. Biotechnol.*, 2014, **98**, 1001–1009.
- 149 X. Hu, J. Li and J. Wang, *ECS Electrochem. Lett.*, 2014, **3**, D13–D15.
- 150 J. Ramyadevi, K. Jeyasubramanian, A. Marikani, G. Rajakumar and A. A. Rahuman, *Mater. Lett.*, 2012, **71**, 114–116.
- 151 T. Tsoncheva, A. Gallo, I. Spassova, M. Dimitrov, I. Genova, M. Marelli, M. Khristova, G. Atanasova, D. Kovacheva and V. Dal Santo, *Appl. Catal. A Gen.*, 2013, **464–465**, 243–252.
- 152 M. Vallet-Regí, F. Balas and D. Arcos, *Angew. Chemie - Int. Ed.*, 2007, **46**, 7548–7558.
- 153 N. T. K. Thanh, N. Maclean and S. Mahiddine, *Chem. Rev.*, 2014, **114**, 7610–7630.
- 154 V. LaMer and R. Dinegar, *J. Am. Chem. ...*, 1950, **72**, 4847–4854.
- 155 V. K. La Mer, *Ind. Eng. Chem.*, 1952, **44**, 1270–1277.

- 156 S. T. Gentry, S. F. Kendra and M. W. Bezpalko, *J. Phys. Chem. C*, 2011, **115**, 12736–12741.
- 157 M. A. Watzky and R. G. Finke, *Chem. Mater.*, 1997, **9**, 3083–3095.
- 158 M. Hölzl, S. Mintova and T. Bein, *Stud. Surf. Sci. Catal.*, 2005, **158**, 11–18.
- 159 K. Norrman, A. Ghanbari-Siahkali and N. B. Larsen, *Annu. Reports Sect. 'C' (Physical Chem.)*, 2005, **101**, 174.
- 160 D. W. Schubert and T. Dunkel, *Mater. Res. Innov.*, 2003, **7**, 314–321.
- 161 2016.
- 162 G. Perego, *Catal. Today*, 1998, **41**, 251–259.
- 163 A. W. Chester and E. G. Derouane, *Zeolite characterization and catalysis: A tutorial*, 2010.
- 164 H. van Bekkum, E. M. Flanigen, P. A. Jacobs and J. C. Jansen, *Introduction to Zeolite Science and Practice-2nd Revised Edition*, Elsevier, 2nd edn., 2001.
- 165 M. Che and J. C. Védrine, *Characterization of Solid Materials and Heterogeneous Catalysts - From Structure to Surface Reactivity*, Wiley-VCH Verlag GmbH & Co. KGaA., 2012.
- 166 G. Pál-Borbély, 2005, **65**, 147–152.
- 167 E. Kissa, *Dispersions: characterization, testing, and measurement*, CRC Press, New York, 1999.
- 168 F. Rouessac and A. Rouessac, *Chemical Analysis: Modern Instrumentation Methods and Techniques*, 2007.
- 169 G. Bergeret and P. Gallezot, *Heterog. Katalyse*, 2002, 738–765.
- 170 D. B. Williams and C. B. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*, 2009, vol. 1–4.
- 171 W. Wan, C. Xiao and X. Zou, *Mesoporous Zeolites Prep. Charact. Appl.*, 2015, 425–460.
- 172 S. Kaliaguine, 1996, vol. 102, pp. 191–230.
- 173 M. Stoecker, *Microporous Mater.*, 1996, **6**, 235–257.
- 174 H. Robson, *Verified synthesis of material - 2nd revised edition*, 2001.
- 175 J. Klinowski, *Anal. Chim. Acta*, 1993, **283**, 929–965.
- 176 R. a. Schoonheydt, *Chem. Soc. Rev.*, 2010, **39**, 5051.
- 177 R. F. Howe, in *Recent Advances and New Horizons in Zeolite Science and Technology*, 1995, vol. 102, pp. 97–139.
- 178 A. Vimont, F. Thibault-Starzyk and M. Daturi, *Chem. Soc. Rev.*, 2010, **39**, 4928–4950.
- 179 F. Zaera, *Chem. Soc. Rev.*, 2014, **43**, 7624–7663.
- 180 S. Thomas, P. Bazin, L. Lakiss, V. De Waele and S. Mintova, *Langmuir*, 2011, **27**, 14689–14695.

Preparation and characterization of metal-containing zeolite crystals

The syntheses methods applied for preparation of zeolites and the methods for their characterization will be described in this chapter.

Information on the structural and physicochemical characteristics of zeolites is of high importance, as it allows the rational development of the materials with the desired properties for advanced applications, such as catalysis, sorption, sensing etc. Since individual analysis technics typically probe only a specific feature of the material, it is necessary to apply the combination of methods to have a balanced description of the system.

Synthesis and post synthesis modification of zeolites

Preparation of pure and copper-containing nanosized LTL zeolite

The precursor suspensions used for preparation of LTL-type zeolite were prepared as follows. In the standard procedure, solution A was prepared by dissolving 2.19 g of KOH (ACS reagent, $\geq 85\%$, pellets, Sigma-Aldrich) and 0.49 $\text{Al}(\text{OH})_3$ (reagent grade, Sigma-Aldrich) in 6.94 g of doubly distilled water at room temperature and stirred until water clear. Solution B was prepared by dissolving of 1.09 g of KOH (ACS reagent, $\geq 85\%$, pellets, Sigma-Aldrich) and 10 g of LUDOX[®] SM 30 colloidal silica (30 wt. % suspension in H_2O , Sigma-Aldrich) in 3.47 g of doubly distilled water at room temperature and stirred until water clear. Solution A was then added drop wise into solution B under vigorous stirring at room temperature to obtain a water clear suspension with the following molar composition: $5 \text{ K}_2\text{O} : 10 \text{ SiO}_2 : 0.5 \text{ Al}_2\text{O}_3 : 200 \text{ H}_2\text{O}$.¹⁵⁸ The as-prepared precursor suspension was aged at room temperature for 24 hours prior to hydrothermal treatment at 170°C for 18 hours. After the crystallization process was accomplished, the nanosized zeolite crystals were recovered by multistep centrifugation

(20000 rpm, 40 min) and washed with doubly distilled water until $\text{pH} = 7 - 8$. Prior to incorporation of copper, the LTL nanosized crystals were stabilized in water suspension with a concentration of solids of 2.5 wt.%. The sample was denoted as parent LTL and was freeze-dried prior to material characterization.

The ion exchange was performed directly in the colloidal suspensions without preliminary calcination of the LTL zeolite. Samples were prepared by mixing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (puriss. p.a., 99-104%, Sigma-Aldrich) (0.1 M) with zeolite suspensions, giving solutions containing 0.3 mmol Cu^{+2}/g zeolite. The ion-exchange process was carried out at room temperature for 2 hours, and then the solutions were purified by multi-step centrifugation to remove the excess of copper ions, and finally re-dispersed in double distilled water to reach a concentration of solids of 2.5 wt.%. Copper exchanged zeolite suspensions were reduced with the following reducing agents under identical conditions: sodium borohydride, triethylamine and hydrazine. In a typical experiment the $\text{Cu}^{+2}/\text{reductant}$ ratio is fixed at 1/1000 to maintain reducing conditions and to avoid oxidation of copper nanoparticles, so complete reduction of copper cations was expected. During the addition of the reductant, the mixture was kept at room temperature under magnetic stirring and N_2 atmosphere, due to the high sensitivity of the copper to oxygen. The samples obtained after reduction with three different reducing agents were further denoted as $\text{Cu}^0\text{-LTL-RA}$.

For the kinetic study of copper nanoparticles growth, the aliquots of suspension were removed periodically from the reaction mixture and freeze-dried with or without washing before further studies. The samples were entitled as $\text{Cu}^0\text{-LTL-x min}$.

The sample was named $\text{Cu}^{2+}\text{-LTL}$ was freeze-dried prior to material characterization.

Reduction of copper cations in zeolite suspensions

Copper exchanged zeolite suspensions were reduced with the following reducing agents under identical conditions: sodium borohydride, triethylamine and hydrazine. In a typical experiment

the Cu^{+2} /reductant ratio is fixed at 1/1000 to maintain reducing conditions and to avoid oxidation of copper nanoparticles, so complete reduction of copper cations was expected. During the addition of the reductant, the mixture was kept at room temperature under magnetic stirring and N_2 atmosphere, due to the high sensitivity of the copper to oxygen. The samples obtained after reduction with three different reducing agents were further denoted as Cu^0 -LTL-RA.

For the kinetic study of copper nanoparticles growth, the aliquots of suspension were removed periodically from the reaction mixture and freeze-dried with or without washing before further studies. The samples were entitled as Cu^0 -LTL-x min.

One-pot synthesis of copper-containing LTL nanocrystals

One-pot synthesis of copper-containing LTL nanocrystals was conducted as follows. Solution A was prepared by dissolving 0.49 g of $\text{Al}(\text{OH})_3$ (reagent grade, Sigma-Aldrich) and 2.5 g of KOH (ACS reagent, $\geq 85\%$, pellets, Sigma-Aldrich) in 4.2 g of doubly distilled water to give a clear suspension; solution B was prepared by adding 10 g of LUDOX[®] SM colloidal silica (30 wt. % suspension in H_2O , Sigma-Aldrich) and 0.8 g of KOH (ACS reagent, $\geq 85\%$, pellets, Sigma-Aldrich) in 4 g of doubly distilled water and stirred until transparent. Solution C was prepared by mixing 0.12 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (puriss. p.a., 99-104%, Sigma-Aldrich) with 2 g of doubly distilled water and 0.34 mL of ammonium hydroxide solution (28%, Prolabo). Then, solution A was mixed with solution C, and the obtained mass was poured slowly into solution B under vigorous stirring. A blue dense gel was formed with the following molar composition: $5 \text{ K}_2\text{O} : 10 \text{ SiO}_2 : 0.5 \text{ Al}_2\text{O}_3 : 1 \text{ CuO} : 200 \text{ H}_2\text{O}$. The gel was aged for 60 h at room temperature under vigorous stirring. In the end the bluish colloidal suspension was subjected to hydrothermal treatment at 170°C for 18 h. After crystallization process occurred, the nanosized crystals were recovered by multistep centrifugation (20000 rpm, 40 min) and washed with doubly distilled water until $\text{pH} = 7$; the sample was entitled. To obtain the H^+ -form of K-Cu-

LTL-IS sample, the latter was subjected to the three – step ion exchange with ammonium chlorite (ACS reagent, $\geq 99.5\%$, Fluka) at 40 °C, followed by purification of the material by multistep centrifugation (20000 rpm, 40 min). The sample was entitled H-Cu-LTL IS.

Preparation of zeolite thin films via spin-coating approach

Thin films of zeolites to flat substrates are prepared by spin coating procedure. An excess amount of a solution is applied to a substrate (in this study using a syringe). The substrate is then rotated at high speed (e.g. up to 10.000 rpm) in order to spread the fluid by centrifugal force. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is volatile, and simultaneously evaporates. The final film thickness is defined by the rotational speed and concentrations of coating suspensions.

Four distinct stages of the spin coating process are shown on the Figure 1.^{159,160}

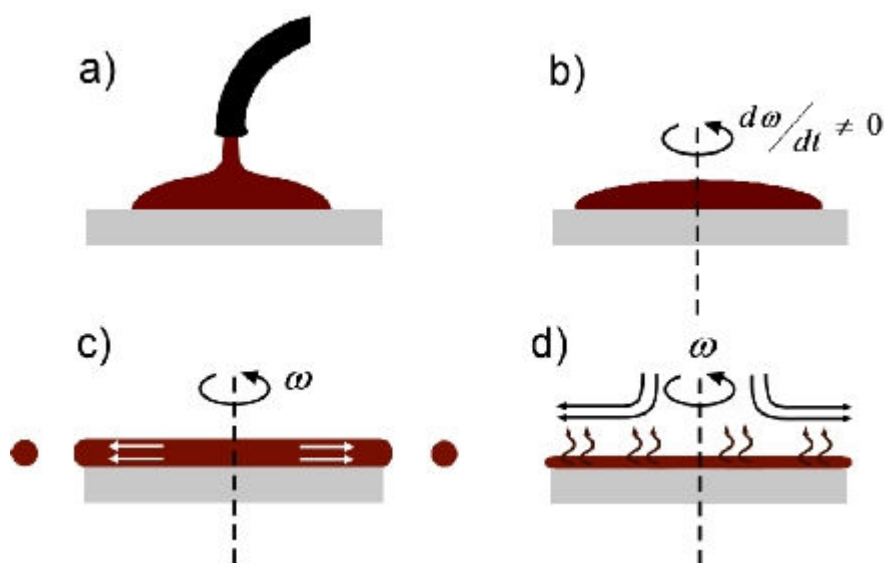


Figure 1 (a) Deposition of the coating fluid onto the wafer or substrate, (b) Acceleration of the substrate up to its final speed, (c) Spinning of the substrate at a constant rate; fluid viscous forces dominate the fluid thinning behavior, (d) Spinning of the substrate at a constant rate; solvent evaporation dominates the coating thinning behavior

There are several specific problems, that might occur during spin-coating. Some of them are presented in Figure 2.

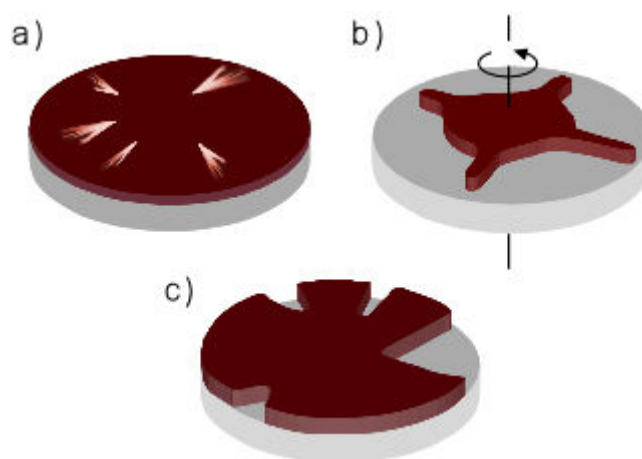


Figure 2 Deviations from the ideal spin coated film. (a) Streaks in the film, probably due to particulate matter on the substrate. (b) Non-uniform liquid expansion during spinning, due to imperfect substrate wetting. (c) Areas of the substrate remain uncoated, which occurs often if the initial liquid volume is too small¹⁶¹

The zeolite films were prepared as follows. The copper-containing zeolite suspensions with a constant concentration of solids (1.5 wt.%) were mixed with the binders (Methylcellulose or Polyvinylpyrrolidone (PVP)) to establish additional stability and high adhesivity in the films. The mixture was dropped onto a preliminarily cleaned with ethanol and acetone Si-wafer. The speed and duration of the spinning rotation were optimized and fixed at 2000 min^{-1} and 30 s, respectively. The coating procedure was repeated until the desired thickness of the film was obtained. At last, a high temperature treatment of the films at 450°C for 1 h was accomplished to enlarge the mechanical properties of the films and to remove the binder. The attained zeolite films have a thickness in the range of 350 – 1500 nm.

Characterization of zeolite suspensions, powders and films

X-Ray Diffraction (XRD)

X-ray diffraction is the most frequently used technique for investigation of the bulk structure and phase purity of zeolites. Their unique structure, in terms of atom positions and unit cell dimensions, is reflected in characteristic positions and relative intensities of the peaks for each phase, a so-called “fingerprint”, distinct from one another allowing phase identification. XRD

provides information about the Bragg angles, θ , of the reflection of an incident monochromatic X-ray beam on crystal planes, according to Bragg's law:

$$n \lambda = 2 \cdot d_{hkl} \sin \theta,$$

where n represents the order of reflection, λ the wavelength of the incident X-ray beam and d the spacing between reflecting crystal planes.¹⁶² The following data can be extracted from a powder diffraction pattern: the topological and long-range structure of a material, the approximate crystal size of the material, strain or stress in the material, the approximate extent of heteroatom substitution, crystallinity, or the presence of stacking disorder.¹⁶³ It is important to note, that the concentration and location of cations at the exchange positions in the material may lead to additional reflections or different intensities of diffraction peaks, whereas the sample microstructure, such as nano size of the crystallites, stacking faults, microstrain, may cause the diffraction peak broadening. In addition, changes in the size of the unit cell resulting from differences in the framework composition influence the positions and the intensity of the XRD peaks.⁸

Generally, the unit cell parameters and the atomic positions of the asymmetric unit can be refined by powder XRD pattern fitting, if a suitable model containing the space group and appropriate starting values is available.¹⁶² Full profile fitting methods calculate theoretical peak profiles and their characteristics until the difference between observed and calculated profiles is minimized. These methods are often used to deconvolute strongly overlapping peaks, to describe minor differences between a reference material and the unknown sample, for unit cell refinements or for quantitative analysis.

In the present study, the crystalline structure of the samples was revealed by using a *PANalytical* X'Pert Pro diffractometer with Cu K α monochromatized radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned in the range 3-80 ° with a step size of 0.02°. The XRD patterns were fit in *PANalytical* X'Pert Pro HighScore Plus software using Pawley fit.

Nitrogen adsorption

According to the IUPAC classification, the diameter of micropores ranges from 0.3 to 2 nm, of mesopores from 2 to 50 nm and of macropores from 50 nm up to 100 μm . Using relatively inert gases such as Ar and N_2 to measure the sorption isotherms at their condensation temperature permits to estimate the size distribution, shape and total volume of the pores.⁸

There are six limiting cases for types of isotherm classified by IUPAC (Figure 3).

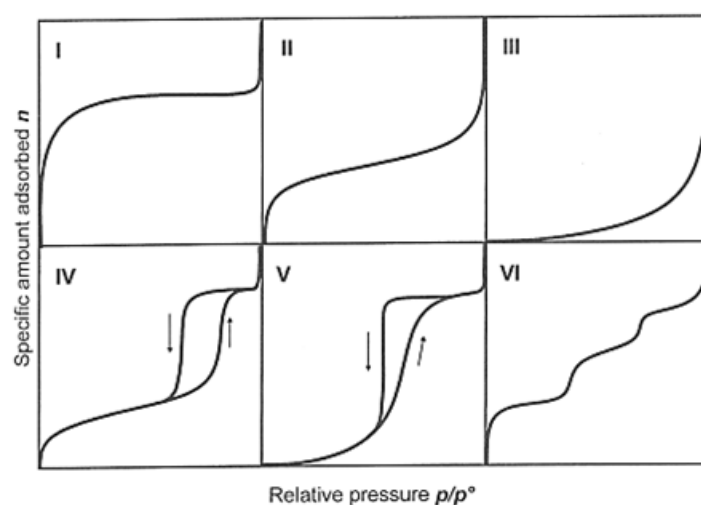


Figure 3 IUPAC classification of sorption isotherms

Microporous solids such as zeolites are usually characterized by Type I isotherms, where the low-pressure adsorption corresponds to filling of the micropore volume. For the nonporous solids stands Type II isotherms, nonporous and non-wetting solids – Type III, mesoporous solids – Type IV, mesoporous non-wetting solids – Type V, and extremely well ordered nonporous systems such as graphite systems where adsorption occurs layer by layer – Type VI. The hysteresis loops observed for the Type IV and Type V isotherms correspond to a capillary condensation phenomena associated with the mesoporosity.^{8,164,165} The characteristics of the different types of isotherms are summarized in Table 1.

Table 1 Type and characteristics of sorption isotherms (adapted from [5])

Type of isotherm	Characteristics
I	Adsorption in micropores
II	Multilayer adsorption on a flat surface
III	Weak gas-solid interactions
IV	Multilayer adsorption and pore condensation
V	Weak gas-solid interactions
VI	Non-porous adsorbent

In the present study, the surface and textural properties of the materials were measured by nitrogen sorption. Nitrogen adsorption/desorption isotherms were obtained using a Micrometrics ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 300 °C under vacuum overnight prior to the measurement. The external surface area ($S_{\text{ext}} / \text{m}^2\text{g}^{-1}$) and micropore volume ($V_{\text{mic}} / \text{cm}^3\text{g}^{-1}$) were estimated by t-plot method based on Harkins-Jura equation using Silica-1000 ($22.1 \text{ m}^2 \text{ g}^{-1}$ assumed) as a reference. The micropore and mesopore size distributions of the samples were estimated Nonlocal Density Functional Theory (NLDFT), and the desorption branch using the Barret-Joyner-Halenda (BJH) algorithm, respectively.⁸

Thermogravimetric analysis

Thermal analysis of solids provides important information about the temperature-dependent properties (heat capacity, thermal stability) of materials and thermally induced processes (dehydration, dehydroxylation, deammoniation, phase transitions, crystal collapse, oxidation, or reduction of lattice constituents). Thermogravimetry (TG) allows to register the change in the weight of a sample as a function of temperature or of time in the case of isothermal measurements. The measurements can be conducted under inert or reactive gases or in vacuum and at wide temperature range with a constant heating rate or using different non-linear

temperature programs. The derivative thermogravimetry (DTG) indicates the rate of the mass loss (dm/dt). Differential thermal analysis (DTA) is based on the measurement of the temperature difference, ΔT , between the sample and an inert material (reference) during a temperature program. In combination with other techniques, TG and DTA may be successfully used to obtain the information on (i) the formation of coke during catalytic processes; (ii) the decomposition behavior of organic guest molecules introduced by adsorption and template molecules occluded during the synthesis in the channel system of zeolites; (iii) the dehydration behavior.¹⁶⁶

The typical TGA/DTA measurement was performed as follows: 10 – 30 mg of sample was introduced in an alumina crucible loaded in the analyzer chamber of a SETSYS 1750 CS evolution instrument (SETARAM). The sample was heated from 30°C to 800°C with a heating ramp of 5°C/min under air (flow rate: 40 mL/min).

Dynamic light scattering

Dynamic Light Scattering (DLS), also known as photon correlation spectroscopy, is the method which utilizes Brownian motion to measure the size of the particles. The velocity of the dispersed particles is related to the fluctuations in the total intensity of the scattered light caused by their Brownian motion, since the smaller particles move more rapidly than large ones.¹⁶⁷

In the following experiments, the particle size distribution (PSD) was determined using a Malvern Zetasizer Nano instrument (scattering angle of 173°, laser wavelength of 632.8 nm, output power of 3 mW). Prior to sample measurement, the samples were repeatedly diluted with doubly distilled water and sonicated prior to the measurements.

Elemental analysis

In general, atomic emission spectroscopy, or optical emission spectroscopy (OES), implicates an elemental analysis, based on registration of the radiation emitted by their atoms present in

an excited state after ionization. To convert a sample to free atoms, excited or ionized, various procedures are employed based upon gas plasmas, sparks, lasers or glow discharges. The most common instruments for OES contain a plasma torch (*inductively coupled plasma* – ICP) that can reach temperatures of up to 8000 K. ICP-OES is the most widely used technique for the determination of the elemental composition of zeolites due to the possibility of the simultaneous determination, with good sensitivity and precision, of most compositional matrix elements of interest, for example silicon, aluminum, phosphorous, titanium, and many others. In ICP-OES atomic vapor is generated from an aqueous sample by plasma as the atomization and excitation source. Each of the elements emits light at the characteristic wavelengths in the ultraviolet or visible region. The concentration of specific element is proportional to the emission intensities in the analyzed sample and can be found by comparison with calibration curve.¹⁶⁸

For all measurements in this study, the elements concentration (e.g. Al, Si, Na, K, Cu etc.) in aqueous solution was performed by inductively coupled plasma-optical emission spectroscopy using an OPTIMA 4300 DV (Perkin–Elmer) instrument. The sample solutions were prepared according to the following procedure: (i) 50 mg of powder was dissolved in 3 ml of hydrofluoric acid (HF) (Sigma Aldrich 40-45 %), then (ii) 0.5 ml of mixture ($\text{HNO}_3 : \text{HCl} \equiv 1:3$ v/v) was added and heated at 100°C for 1 h in polytetrafluoroethylene (PTFE) bottle, and (iii) finally 10 ml of double deionized water and 2.8 g of boric acid (H_3BO_3) were added. The resulted solution was transferred to PTFE volumetric flask (100 mL) and diluted with double deionized water to 100 ml, and shaken until full dissolution of the sample.

Electron microscopy

Electron microscopy is a powerful tool for structural characterization of porous materials, because it provides a direct observation of catalyst morphology with a magnification tunable in the range $10^{-4} - 10^{-10}$ m. There are many different electron microscopy techniques available,

such as scanning electron microscopy (SEM), electron diffraction (ED), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM). In addition, an energy-dispersive X-ray spectroscopy (EDS) device attached to an electron microscope can provide the chemical information of the sample. Accurate data on the shape, size and spatial arrangement of particles of supports and active phases can be obtained. Structural information such as symmetry and unit cell parameters of crystallites, crystal orientations and lattice defects can also be obtained by electron diffraction and lattice imaging techniques.¹⁶⁹

The advantage of using electrons as ionizing radiation is that it produces a wide range of secondary signals from the specimen that can provide additional information about the specimen. Some of the secondary signals are shown in the Figure 4.^{170,171}

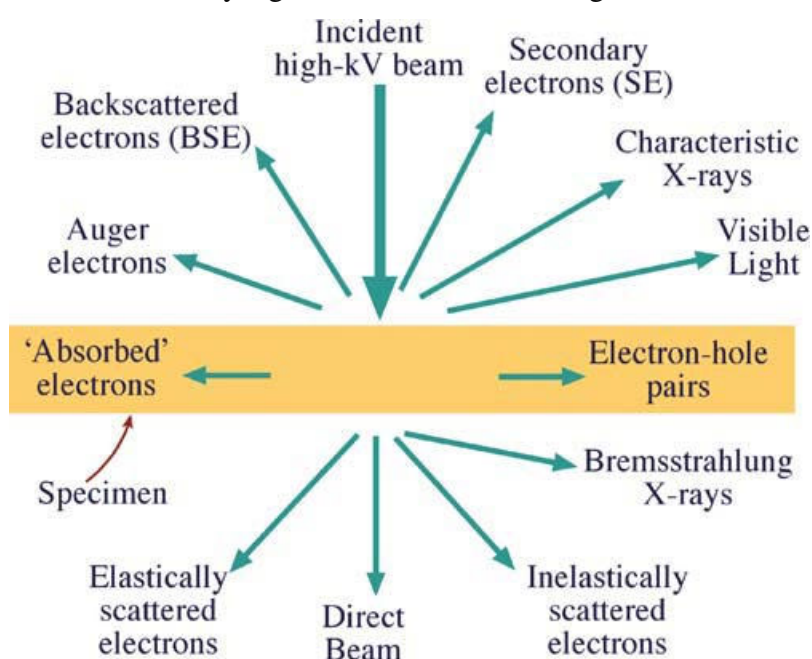


Figure 4 Signals generated when a high-energy beam of electrons interacts with a thin specimen. The directions shown for each signal do not always represent the physical direction of the signal, but indicate, in a relative manner, where the signal is strongest or where it is detected (reprinted from [170])

a. Scanning electron microscopy

SEM is an important technique for the characterization of conventional zeolites and mesoporous zeolites. SEM makes available the information on the size, morphology, and point group symmetry of the crystals. With the development of low-voltage electron beam

configuration, mesopore openings on the surfaces of zeolite crystals can be directly observed by SEM. By combining the appropriate sample preparation techniques such as cross-section polisher using argon ion beam, SEM can also be used for studying the interior structure of the crystals.¹⁷¹ SEM has some advantages over TEM as SEM has a larger depth of focus for the determination of crystal morphology and fine surface structures so that surface topology can be observed as different contrast in the image by a relatively simple experiment.⁸

For the SEM characterization in this study, small amounts of zeolite suspension or films were placed on a specimen holder using double stick carbon tapes. To improve the electrical conductivity of the sample, they were coated with platinum using CRESSINGTON 108 auto evaporative coating machine. SEM micrographs were recorded with TESCAN Mira field-emission scanning electron microscope operating at 15 – 30 kV.

b. Transmission electron microscopy

TEM is used for structural analysis of zeolites and mesoporous zeolite crystals at higher resolution (up to atomic) as compared with SEM. High-resolution transmission electron microscopy (HRTEM) images are related to the projected electrostatic potential of the materials. Electrons can be focused by magnetic lenses, and thus HRTEM images can be obtained. Both the amplitude and the phase information of the crystal structure can be extracted from the HRTEM images and used to solve the structures of complex zeolite materials and ordered mesoporous silica materials. The HRTEM images provide direct, intuitive representation of the object in real space.¹⁷¹ The images are formed either with the unscattered, transmitted electrons or the scattered electrons, resulting in bright- and dark-field images, respectively. The point-to-point resolution depends mainly on the size of the electron probe. The point-to-point resolution of bright field images is not as good as in TEM, but STEMs are equipped with annular detectors that allow the efficient collection of electrons scattered at high angles, thus allowing high-angle annular dark field (HAADF) imaging. It is important to know,

that porous materials are often very electron beam sensitive. That is why low electron doses are employed to minimize the radiation damage; thus, the signal-to-noise ratio and resolution of the obtained HRTEM images are usually very low.

The HRTEM and EDX studies were performed using a Tecnai G2 30 UT (LaB₆) microscope operated at 300 kV with 0.17 nm point resolution and equipped with a EDAX EDX detector. Besides, the size and distribution of copper particles were studied by high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). High angle annular dark field and annular bright field (ABF) – scanning TEM studies were performed using a JEOL ARM200F cold FEG double aberration corrected electron microscope operated at 200 kV and equipped with a large solid-angle centurio EDX detector and Quantum EELS spectrometer.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is one of the most widely used tools of surface analysis of zeolites.^{172,173} X-ray photoelectron spectroscopy is a technique whereby a beam of monoenergetic X-ray photons interacts with the atoms of a solid.

In addition to the valence electrons, each atom present in the surface (except H₂ and He) possesses core electrons not directly involved in the bonding. The so-called 'binding energy' (E_b) of each core electron is characteristic of the individual atom to which it is bound. In the basic XPS experiment, the sample surface is irradiated by a source of low-energy X-rays under ultra-high vacuum. Photoionization then takes place in the sample surface (depth of analysis between 1.5 and 6nm). The resultant photo-electrons have a kinetic energy (E_k) in the range of 20 to 2000 eV.^{172,173}

If the collided atom lies too deep below the surface, all emitted photoelectrons will undergo inelastic collisions with other atoms before they can exit from the solid. By contrast if the atom is located within a short distance from the surface, the extracted photoelectrons have a non-zero probability to leave the solid without having experienced a collision.¹⁷²

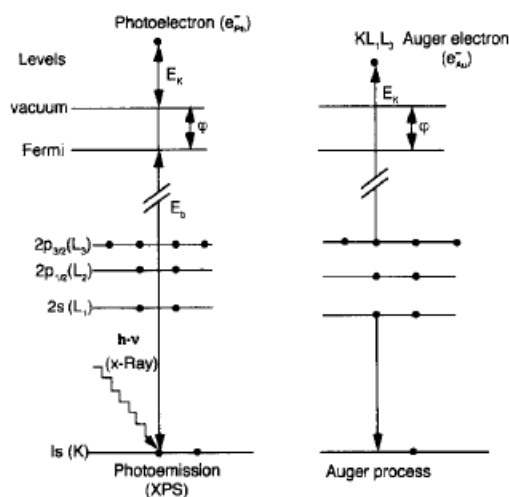


Figure 5 Photoemission (XPS) and the Auger process; adapted from [14]

The left side of the Figure 5 exhibits an absorbed incident X-ray photon and an emitted photoelectron. Measurement of its kinetic energy allows one to calculate the binding energy of the photoelectron. The atom stays behind as an unstable ion with a hole in one of the core levels. On the right, the excited ion relaxes by filling the core hole with an electron from a higher shell. The energy released by this transition is taken up by another electron, the Auger electron, which leaves the samples with an element-specific kinetic energy.¹⁷³

Solid-state nuclear magnetic resonance (MAS NMR) spectroscopy

Solid-state NMR is a complementary technique to XRD, since XRD provides information about the long-range ordering and periodicities, while NMR allows investigations on the short-range ordering and structure. During recent years, several techniques have been developed for averaging chemical shift anisotropy (CSA), dipolar and quadrupolar interactions which lead to excessive line broadening to zero, or reduce them to the isotropic values, allowing the registration of high-resolution NMR spectra of solids. Depending on the nuclear spin I responsible for the magnetic dipole moment, different line narrowing techniques are required to reach highly resolved solid-state NMR spectra of zeolites. In the case of spin $I = 1/2$, the application of the conventional magic angle spinning (MAS) technique leads to an averaging of the most important nuclear interactions, such as anisotropic chemical shielding and dipolar

interactions. Isotopes with nuclear spin $I > 1/2$ are additionally characterized by an electric quadrupole moment. These nuclei are involved in quadrupolar interactions and often require more sophisticated solid-state NMR techniques, such as high-field MAS NMR, double-oriented rotation (DOR), and multiple-quantum MAS (MQMAS) NMR spectroscopy.

All the relevant basic nuclei contributing to the framework of zeolites and AlPO_4 molecular sieves can be detected in NMR by their natural isotopes: ^{29}Si , ^{27}Al , ^{31}P and ^{17}O . Both ^{27}Al and ^{31}P spectra are easily detected within reasonable time, however, ^{27}Al has a quadrupole moment which can cause line broadening due to interaction with the electric field gradient. Investigations of ^{17}O NMR can be done by using enriched material, since the natural abundance is low. ^{29}Si chemical shift is sensitive to the number and type of tetrahedrally coordinated atoms connected to a given SiO_4 unit $\text{Si}(\text{n Al})$, with $n = 0, 1, 2, 3$ or 4 , where n indicates the number of Al atoms sharing oxygens with the SiO_4 tetrahedron. Differences in chemical shifts between $\text{Si}(\text{n Al})$ and $\text{Si}(\text{n}+1 \text{ Al})$ are about 5-6 ppm. Furthermore, ^{29}Si MAS NMR spectra can be used to calculate the framework Si / Al ratio from the NMR signal intensities. ^{27}Al NMR spectra reveal the existence of extra-framework Al (about 0 ppm) besides the lattice aluminum (tetrahedrally coordinated Al at about 40-65 ppm).

Solid-state ^1H NMR of protons, OH groups, adsorbed water, organic sorbates and probe molecules containing hydrogen in microporous and mesoporous molecular sieves has been developed as a usable method for getting information about different kinds of hydrogens in terminal or bridging OH groups, varying environments for hydrogen containing probe molecules and acidity investigations as well. Other nuclei which can substitute the usual framework elements in microporous and mesoporous materials can be probed by solid-state NMR, for example, ^{11}B , ^{73}Ge and $^{69,71}\text{Ga}$. Also, some extra-framework cations, like ^7Li , ^{23}Na , ^{39}K , ^{133}Cs or ^{195}Pt , are suitable for NMR measurements. However, most of those elements possess a quadrupole moment which usually limits the application.^{163,174,175}

UV-visible spectroscopy

Ultraviolet–visible–near infrared spectroscopy (UV-VIS-NIR) covers the wavelength range 200–2500 nm or in wavenumbers 50 000–4000 cm^{-1} . This range is usually divided in three regions: UV: 200–400 nm or 50 000–25 000 cm^{-1}

VIS: 400–800 nm or 25 000–12 500 cm^{-1}

NIR: 800–2500 nm or 12 500–4000 cm^{-1}

The application of UV-VIS-NIR spectroscopy in research on heterogeneous catalysts is related to the study of transition metal ions, rare earth metal ions, adsorbed molecules, molecular ions and radicals; and the support, which can be amorphous metal oxides with a high surface area or porous crystalline materials such as zeolites and mesoporous materials. The electronic transitions that may be involved in UV-VIS-NIR spectroscopy are summarized in Table 2.¹⁷⁶

Table 2 Electronic transitions probed in heterogeneous catalysts

Center	Transition
Transition metal ion	D–d, metal-to-ligand charge transfer; ligand-to-metal charge transfer
Rare earth ion	F–f, f–d
Molecules, radicals, molecular ions	N–p*; p–p*
Support	Band gap, impurities, defects

UV–vis spectroscopy is one of the primary methods to verify framework substitution of transition metal cations into zeolites. The coordination or valence of the ion must be unique to the framework species and different from extra-framework species. The valence and coordination of transition metals introduced into zeolites via ion exchange can be evaluated by UV–vis as well. Typically, changes in coordination, for instance, through hydration and dehydration, can be observed. Moreover, through the adsorption of suitable molecules, the location and mobility of the ions may be probed.

To quantify the concentrations of an absorbing species in solution the Beer-Lambert law is used where the amount of light absorbed is proportional to the number of absorbing molecules through which the light passes.^{165,168}

In this study, the kinetics of copper nanoparticles growth was followed by in-situ UV-Vis spectroscopy. Electronic absorption spectra of diluted suspensions were recorded on a Varian Cary 4000 UV-Vis-NIR spectrometer. The measurements were performed in absorbance mode. Also, the UV-vis spectra of the self-supported pellets of the copper-containing samples were recorded in diffuse reflectance mode.

Electron paramagnetic resonance (EPR)

Using electron paramagnetic resonance (EPR) in principle can be used to observe any species containing one or more unpaired electrons. For zeolites, this covers paramagnetic transition metal or rare earth ions, solid state defects which are paramagnetic, and inorganic or organic radicals. This sensitivity of the method imposes the need for caution in interpreting weak signals, which can be caused by trace level impurities irrelevant to the chemistry being studied.¹⁷⁷

Continuous wave CW-EPR spectra were recorded at the X band (9.5 GHz) with a Bruker ELEXSYS E500 spectrometer equipped with a high-sensitivity 4122SHQE/0111 microwave cavity and with helium flow cryostat for low temperature measurements.

Fourier transformed infrared spectroscopy (FTIR)

FTIR spectroscopy is one of the most adapted tools for extensive characterization of the catalysts active sites, being extremely sensitive to the molecular vibrations and able to discriminate the different geometrical distortions of the molecules according to the adsorption state on a site. The region of interest is mid-IR region, which covers the range of the electromagnetic spectrum from 25 to 2.5 μm , that is, in wavenumber terms, from 400 to 4000 cm^{-1} . The frequency of the radiation is denoted by ν , and the wavelength is $\lambda=c/\nu$.

The best way to identify the potential active sites by IR spectroscopy is the direct recognition of their IR fingerprint. If direct detection is not possible, the adsorption of probe molecules, which provides IR spectra specific to the interaction with a single site can be employed, as the most common the most used technique. However, it should be stressed that any probe molecule generates a perturbation of the surface of the catalysts: indirect perturbations such as electron withdrawing effect, or direct perturbations like chemical reactions (protonation, electron transfer, decomposition etc.). In this case, the best way is to use the molecule that acts as a reactant during the chosen catalytic reaction.¹⁷⁸

The easiest way to measure the IR spectrum of a solid is to place the powder as a suspension in a neutral oil (Nujol) or to disperse it (0.5–1%) in potassium bromide (KBr). The resulting powder is pressed from a pellet and placed directly in the IR beam. Such a method cannot be used for characterizing the surface properties of catalysts (e.g., with probe molecule adsorption studies), but can provide interesting information about the structure of the materials.¹⁶⁵

a. In situ FTIR spectroscopy

Studies of adsorption and catalytic reactions on catalytic surfaces exposed to gas-phase mixtures are the most common. To address surface characterization under more realistic catalytic conditions, IR spectroscopic studies can be performed in situ, under conditions resembling those encountered in catalysis. Characterization work on surface properties is performed in the transmission mode. This is generally done with a self-supporting wafer of the pure solid, that is, without any KBr matrix that would contaminate the surface and introduce external ions. This wafer must be very thin (in this study all pellets are 20 mg) so that it remains IR transparent, and must only be pressed very gently, so that neither gas diffusion nor the structure of the solid are perturbed.^{165,179}

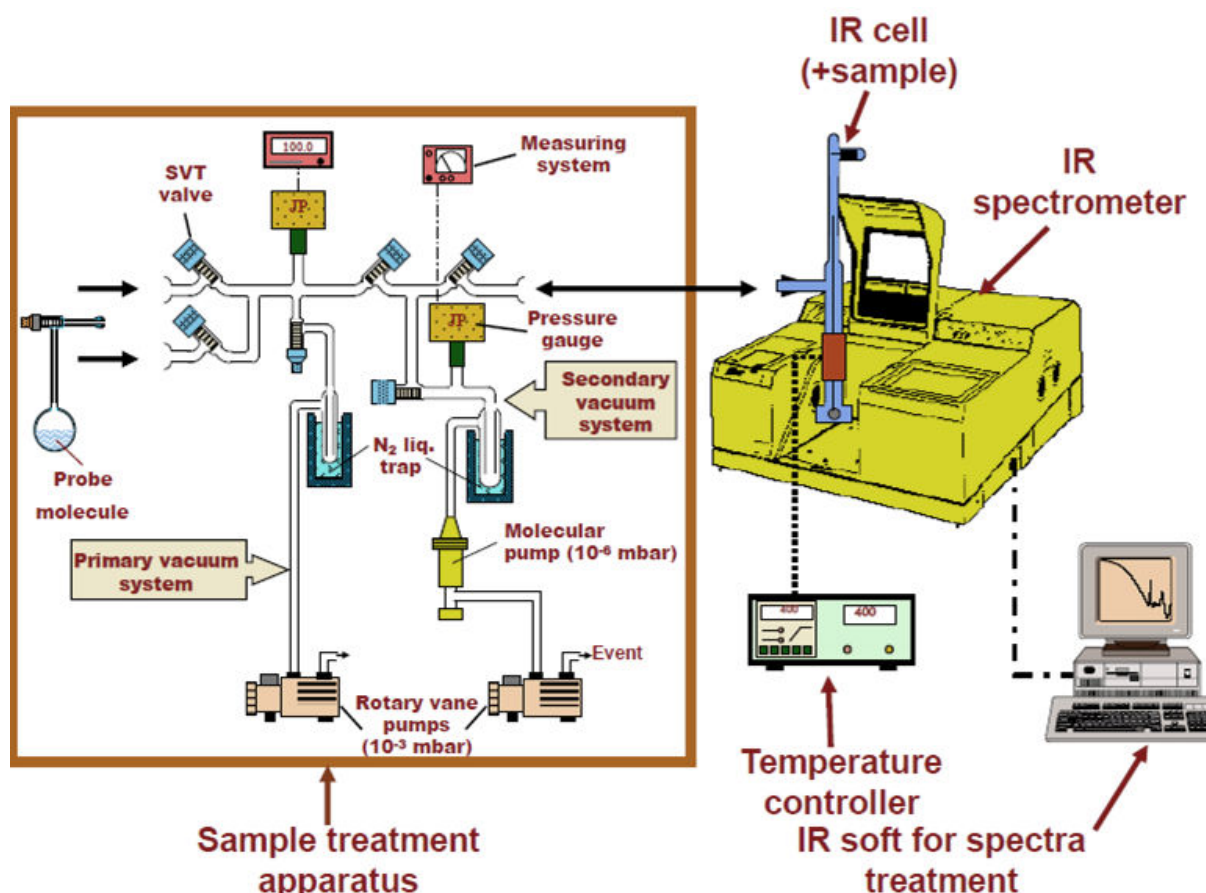


Figure 6 *In situ* FTIR set-up

Prior to all *in situ* FTIR measurement, the solid materials were grinded and pressed into self-supported thin pellets with the mass of 20 mg.

To study CO and NO adsorption, the disks were placed in a standard LCS *in-situ* FTIR set-up (Figure 6) pretreated under vacuum ($\sim 10^{-6}$ Torr) or under chosen atmosphere (H_2 , O_2) at 673 (723) K for 5 hours with ramp of 1.3 K/min. After cooling down to room temperature, the spectrum of the surface was recorded for further use as a reference at room temperature. After, the cell was cooled down to 100 K with liquid nitrogen, the spectrum of the surface was then again collected to be used as a reference at 100 K. The small doses of gas were gradually introduced in the cell at 100K and the spectra were recorded. In the end, the equilibrium pressure of gas was introduced in the cell to collect the spectrum, then the desorption under vacuum at 100K and at RT was performed.

To conduct the temperature programmed desorption of pyridine to probe the acid sites of the materials, the samples were placed in a standard LCS *in-situ* FTIR set-up pretreated under vacuum ($\sim 10^{-6}$ Torr) at 673 (723) K for 5 hours with ramp of 1.3 K/min. After cooling down to 423 K, the surface was recorded, 1 Torr of pyridine was introduced into the system for 40 min to saturate the material. Pyridine was desorbed and spectra were collected at 423, 473, 523, 573, 623, 673 K.

The cell was equipped with two ports for the introduction of probe molecules and a calibrated small volume between two valves, allowing introduction of known amounts of the probe molecules. The cell was, as well, equipped with the manometer to measure the residuals of the gas in the cell after adsorption on the surface before introduction of each new dose of gas.

The OMNIC 8 software was used for data processing.

b. Operando reflection FTIR spectroscopy

The detection of CO with prepared films was followed by *operando* IR spectroscopy using the setup described elsewhere.^{82,145,180} The set-up is composed of a sample compartment (IR reactor cell) and a gas flow system. The IR reactor cell consists of a modified diffuse reflectance IR cell (diffuse reflectance accessory, Pike) and an environmental chamber to study the supported this films under control gas flow and temperature (Figure 7).

The IR reactor cell is equipped with a heating system working at temperatures up to 350 °C, where an air cooling system is used to protect both the KBr windows and the Viton o-rings. All experiments were carried out at atmospheric pressure. Prior to the detection, the as-prepared zeolite films were subjected to activation in the *in-situ* IR reactor cell with 10% H₂ in argon at 350°C (heating rate of 1°C /min). CO was prepared and sent independently to the IR reactor cell. The gas compositions used for the experiments are as follows: activation flow, Ar with a total flow of 20 cm³/min; reaction flow CO with a concentration of 1 – 100 ppm diluted in Ar

with a total flow of 20 cm³/min. The IR spectra were collected in a continuous mode (32 scans/spectrum) with a Tensor 27 spectrometer (Bruker) equipped with a DTGS detector.

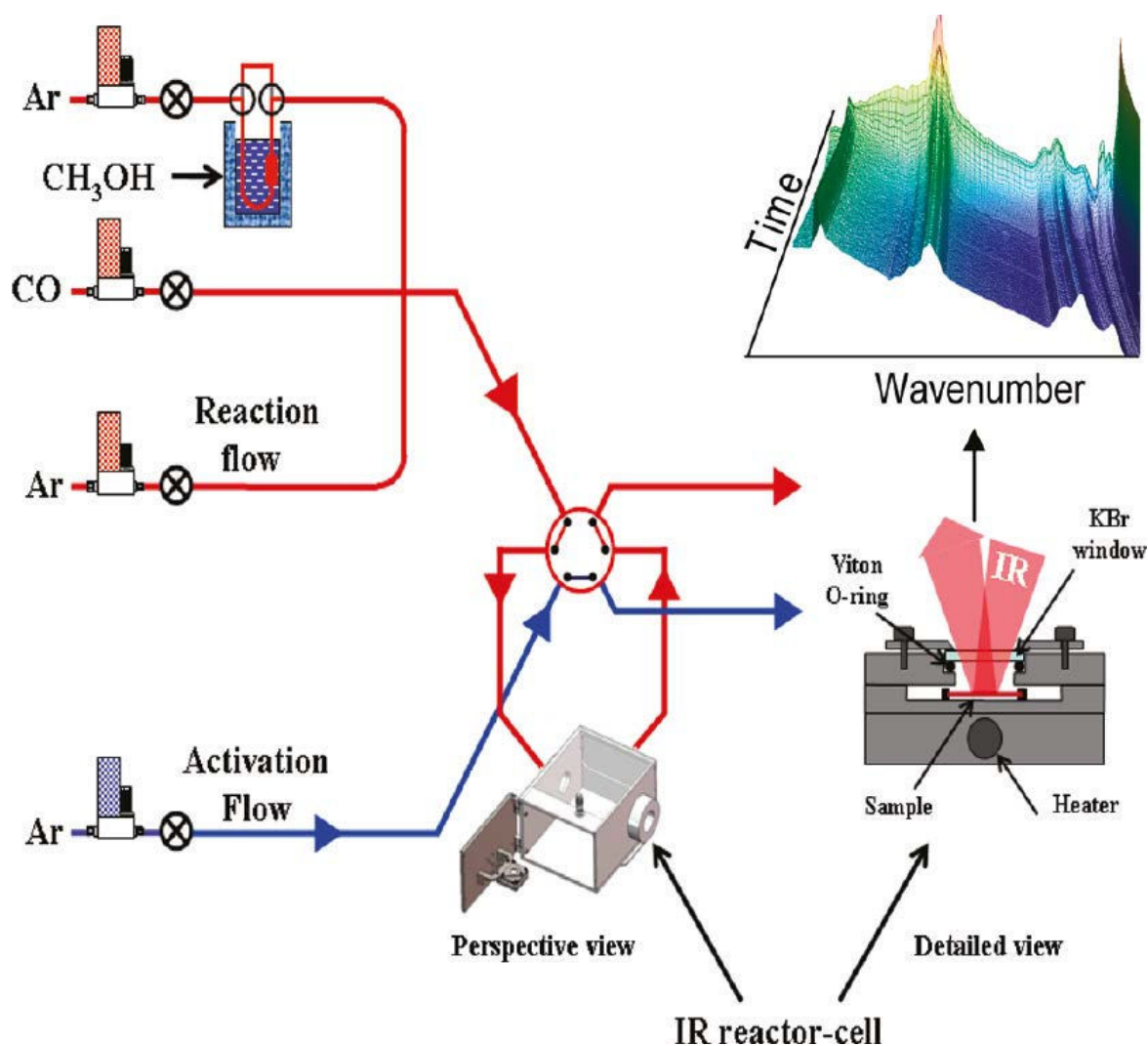


Figure 7 Experimental setup used for CO probing: in situ IR reactor cell for characterization of thin films combined with IR operando gas system (adapted from [180])

References

- 1 A. Steinfeld, C.- Zurich and R. Palumbo, *Encycl. Phys. Sci. Technol.*, 2001, **15**, 237–256.
- 2 S. Licht, *Chem. Commun. (Camb)*., 2005, **2005**, 4635–4646.
- 3 R. R. Conry, *Encycl. Inorg. Chem.*, 2006, 1–19.
- 4 M. B. Gawande, A. Goswami, F.-X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril and R. S. Varma, *Chem. Rev.*, 2016, **116**, 3722–3811.
- 5 C. Martínez and A. Corma, *Compr. Inorg. Chem. II*, 2013, 103–131.
- 6 J. Cejka, A. Corma and S. Zones, Eds., *Zeolites and Catalysis. Synthesis, Reactions and Applications*, Wiley-VCH Verlag GmbH & Co. KGaA., 2010.
- 7 J. Weitkamp and L. Puppe, Eds., *Catalysis and Zeolites. Fundamentals and Applications*, Springer-Verlag Berlin Heidelberg, 1st editio., 1999.
- 8 J. Cejka, H. van Bekkum, A. Corma and F. Schueth, *Introduction to Zeolite Science and Practice- 3rd Revised Edition*, Elsevier, 3rd editio., 2007.
- 9 P. Eliášová, M. Opanasenko, P. S. Wheatley, M. Shamzhy, M. Mazur, P. Nachtigall, W. J. Roth, R. E. Morris and J. Čejka, *Chem. Soc. Rev.*, 2015.
- 10 A. Primo and H. Garcia, *Chem. Soc. Rev.*, 2014, **43**, 7548–7561.
- 11 S. M. Auerbach, K. A. Carrado and P. K. Dutta, *Handbook of zeolite science and technology*, CRC Press, 2004, vol. 2004.
- 12 J. Weitkamp, *Solid State Ionics*, 2000, **131**, 175–188.
- 13 C. Martinez and J. Perez-Pariente, Eds., *Structural Chemistry and Properties of Zeolites*, 1st edn., 2011.
- 14 P. Payra and P. K. Dutta, in *Handbook of Zeolite Science and Technology*, 2003.
- 15 *Catalysis and Zeolites*, 1999.
- 16 D. H. Everett, *Pure Appl. Chem.*, 1973.
- 17 C. Baerlocher, L. McCusker and D. Olson, *Atlas of zeolite framework types*, 2007, vol. 12.
- 18 J. Li, A. Corma and J. Yu, *Chem. Soc. Rev.*, 2015.
- 19 C. S. Cundy and P. a Cox, 2003, **103**, 663–702.
- 20 G. Perego, G. Bellusi, C. Corno, M. Taramasso, F. Buonomo and A. Esposito, *Stud. Surf. Sci. Catal.*, 1986, **28**, 129–136.
- 21 G. Bellussi and M. S. Rigutto, in *Advanced Zeolite Science and Applications*, eds. J.C. Jansen, M. Stocker, H. G. Karge and J. Weitkamp, Elsevier B.V, 1994, vol. 85, pp. 177–213.
- 22 K. G. Ione, L. A. Vostrikova and V. M. Mastikhin, *J. Mol. Catal.*, 1985, **31**, 355–370.
- 23 K. G. Ione and L. A. Vostrikova, *Russ. Chem. Rev.*, 1987, **56**, 393–427.
- 24 B. Sulikowski, *Heterog. Chem. Rev.*, 1996, **3**, 203–268.
- 25 G. Coudurier, A. Auroux, J. C. Vedrine, R. D. Farlee, L. Abrams and R. D. Shannon, *J. Catal.*, 1987, **108**, 1–14.
- 26 S. Bordiga, A. Damin, F. Bonino, G. Ricchiardi, C. Lamberti and A. Zecchina, *Angew. Chemie - Int. Ed.*, 2002, **41**, 4734–4737.
- 27 G. Ricchiardi, A. Damin, S. Bordiga, C. Lamberti, G. Spanò, F. Rivetti and A. Zecchina, *J. Am. Chem. Soc.*, 2001, **123**, 11409–11419.
- 28 R. Millini, E. Previde Massara, G. Perego and G. Bellussi, *J. Catal.*, 1992, **137**, 497–503.
- 29 G. Tozzola, M. a. Mantegazza, G. Ranghino, G. Petrini, S. Bordiga, G. Ricchiardi, C. Lamberti, R. Zulian and A. Zecchina, *J. Catal.*, 1998, **179**, 64–71.
- 30 C. Lamberti, S. Bordiga, A. Zecchina, A. Carati, N. N. Fitch, G. Artioli, G. Petrini, M. Salvalaggio and G. L. L. Marra, *J. Catal.*, 1999, **183**, 222–231.

- 31 S. Bordiga, F. Boscherini, S. Coluccia, F. Genonic, C. Lamberti, G. Leofanti, L. Marchese, G. Petrini, G. Vlaic and A. Zecchina, *Catal. Letters*, 1994, **26**, 195–208.
- 32 R. Fricke, H. Kosslick, G. Lischke and M. Richter, *Chem. Rev.*, 2000, **100**, 2303–2405.
- 33 C. Lamberti, G. T. Palomino, S. Bordiga, A. Zecchina and G. Span, *Science (80-.)*, 1999, **63**, 213–216.
- 34 C. Otero Areán, G. Turnes Palomino, F. Geobaldo and a. Zecchina, *J. Phys. Chem.*, 1996, **100**, 6678–6690.
- 35 X. Liu and J. Klinowski, *J. Phys. Chem.*, 1992, **311**, 3403–3408.
- 36 C. R. Bayense, A. P. M. Kentgens, J. W. De Haan, L. J. M. Van de Ven and J. H. C. Van Hooff, *J. Phys. Chem.*, 1992, **96**, 775–782.
- 37 G. Berlier, G. Spoto, S. Bordiga, G. Ricchiardi, P. Fisicaro, A. Zecchina, I. Rossetti, E. Selli, L. Forni, E. Giamello and C. Lamberti, *J. Catal.*, 2002, **208**, 64–82.
- 38 S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola and G. Vlaic, *J. Catal.*, 1996, **158**, 486–501.
- 39 A. Zecchina, F. Geobaldo, C. Lamberti, S. Bordiga, G. Turnes Palomino and C. Otero Arean, *Catal. Letters*, 1996, **42**, 25–33.
- 40 R. Szostak and T. L. Thomas, *J. Catal.*, 1986, **100**, 555–557.
- 41 R. Kumar and P. Ratnasamy, *J. Catal.*, 1990, **121**, 89–98.
- 42 S. N. Talapaneni, J. Grand, S. Thomas, H. A. Ahmad and S. Mintova, *Mater. Des.*, 2016, **99**, 574–580.
- 43 S. Tolborg, A. Katerinopoulou, D. D. Falcone, I. Sádaba, C. M. Osmundsen, R. J. Davis, E. Taarning, P. Fristrup and M. S. Holm, *J. Mater. Chem. A*, 2014, **2**, 20252–20262.
- 44 T. Iida, A. Takagaki, S. Kohara, T. Okubo and T. Wakihara, *ChemNanoMat*, 2015, **1**, 155–158.
- 45 H. Y. Luo, L. Bui, W. R. Gunther, E. Min and Y. Román-Leshkov, *ACS Catal.*, 2012, **2**, 2695–2699.
- 46 W. R. Gunther, Y. Wang, Y. Ji, V. K. Michaelis, S. T. Hunt, R. G. Griffin and Y. Román-Leshkov, *Nat. Commun.*, 2012, **3**, 1109.
- 47 S. Roy, K. Bakhmutsky, E. Mahmoud, R. F. Lobo and R. J. Gorte, *ACS Catal.*, 2013, **3**, 573–580.
- 48 A. Corma, L. T. Nemeth, M. Renz and S. Valencia, *Nature*, 2001, **412**, 423–425.
- 49 R. Szostak, *Molecular Sieves. Principles of Synthesis and Identification*, 1988.
- 50 R. Aiello, J. B. Nagy, G. Giordano, A. Katovic and F. Testa, *Comptes Rendus Chim.*, 2005, **8**, 321–329.
- 51 V. Valtchev and L. Tosheva, *Chem. Rev.*, 2013, **113**, 6734–6760.
- 52 S. Mintova and E.-P. Ng, in *Comprehensive Inorganic Chemistry II: From Elements to Applications*, 2013, vol. 5, pp. 285–302.
- 53 S. C. Larsen, *J. Phys. Chem. C*, 2007, **111**, 18464–18474.
- 54 S. Mintova, J. Grand and V. Valtchev, *Comptes Rendus Chim.*, 2016, **19**, 183–191.
- 55 M. Zaarour, B. Dong, I. Naydenova, R. Retoux and S. Mintova, *Microporous Mesoporous Mater.*, 2014, **189**, 11–21.
- 56 S. Mintova, M. Jaber and V. Valtchev, *Chem. Soc. Rev.*, 2015, **44**, 7207–7233.
- 57 C. Madsen, C. Madsen and C. J. H. Jacobsen, *Chem. Commun.*, 1999, 673–674.
- 58 Y. Pan, M. Ju, J. Yao, L. Zhang and N. Xu, *Chem. Commun. (Camb.)*, 2009, 7233–5.
- 59 C. Jo, J. Jung, H. S. Shin, J. Kim and R. Ryoo, *Angew. Chemie - Int. Ed.*, 2013, **52**, 10014–10017.
- 60 S. Askari, S. Miar Alipour, R. Halladj and M. H. Davood Abadi Farahani, *J. Porous Mater.*, 2012, **20**, 285–302.
- 61 J. Gascon, F. Kapteijn, B. Zornoza, V. Sebastián, C. Casado and J. Coronas, *Chem.*

- Mater.*, 2012, **24**, 2829–2844.
- 62 N. Kosinov, V. G. P. Sripathi and E. J. M. Hensen, *Microporous Mesoporous Mater.*, 2014, **194**, 24–30.
 - 63 N. Kosinov, C. Auffret, V. G. P. Sripathi, C. Gücüyener, J. Gascon, F. Kapteijn and E. J. M. Hensen, *Microporous Mesoporous Mater.*, 2014, **197**, 268–277.
 - 64 D. W. Breck, *J. Chem. Educ.*, 1964, **41**, 678–689.
 - 65 K. Li, J. Valla and J. Garcia-Martinez, *ChemCatChem*, 2014, **6**, 46–66.
 - 66 I. Fechete, Y. Wang and J. C. V??drine, *Catal. Today*, 2012, **189**, 2–27.
 - 67 R. Moos, *Sensors*, 2010, **10**, 6773–6787.
 - 68 T. Bein and S. Mintova, *Zeolites and Ordered Mesoporous Materials: Progress and Prospects*, Elsevier, 2005, vol. 157.
 - 69 S. Mintova and T. Bein, *Microporous Mesoporous Mater.*, 2001, **50**, 159–166.
 - 70 Y. Zheng, X. Li and P. K. Dutta, *Sensors*, 2012, **12**, 5170–5194.
 - 71 T. Baimpos, L. Gora, V. Nikolakis and D. Kouzoudis, *Sensors Actuators A Phys.*, 2012, **186**, 21–31.
 - 72 D. J. Wales, J. Grand, V. P. Ting, R. D. Burke, K. J. Edler, C. R. Bowen, S. Mintova and A. D. Burrows, *Chem. Soc. Rev.*, 2015.
 - 73 M. Vilaseca, J. Coronas, A. Cirera, A. Cornet, J. R. Morante and J. Santamaría, *Catal. Today*, 2003, **82**, 179–185.
 - 74 K. Sahner, G. Hagen, D. Schönauer, S. Reiß and R. Moos, *Solid State Ionics*, 2008, **179**, 2416–2423.
 - 75 C. M. Lew, R. Cai and Y. Yan, *Acc. Chem. Res.*, 2010, **43**, 210–219.
 - 76 M. Moothanchery, I. Naydenova, S. Mintova and V. Toal, *Opt. Express*, 2011, **19**, 25786–25791.
 - 77 US pat., 20090130154 A1, 2009.
 - 78 S. E. Lehman and S. C. Larsen, *Environ. Sci. Nano*, 2014, **1**, 200–213.
 - 79 N. Tirtaatmadja, G. Mortimer, E.-P. Ng, H. A. Ahmad, S. Mintova, V. Serpooshan, R. F. Minchin and M. Mahmoudi, *J. Iran. Chem. Soc.*, 2014, **12**, 317–323.
 - 80 A. Petushkov, J. Intra, J. B. Graham, S. C. Larsen and A. K. Salem, *Chem. Res. Toxicol.*, 2009, **22**, 1359–1368.
 - 81 J. A. Litch and R. A. Bishop, *Wilderness Environ. Med.*, 2000, **11**, 189–191.
 - 82 T. Babeva, H. Awala, M. Vasileva, J. El Fallah, K. Lazarova, S. Thomas and S. Mintova, *Dalton Trans.*, 2014, **43**, 8868–8876.
 - 83 E. Leite, T. Babeva, E. P. Ng, V. Toal, S. Mintova and I. Naydenova, *J. Phys. Chem. C*, 2010, **114**, 16767–16775.
 - 84 A. Seidel, J. Loos and B. Boddenberg, *J. Mater. Chem.*, 1999, 2495–2498.
 - 85 V. Gurin and V. Petranovskii, *Stud. Surf. Sci. Catal.*, 2004, **154**, 1661–1669.
 - 86 V. S. Gurin, V. P. Petranovskii, M. -a. Hernandez, N. E. Bogdanchikova and a. a. Alexeenko, *Mater. Sci. Eng. A*, 2005, **391**, 71–76.
 - 87 A. Kharchenko, O. I. Lebedev, V. Zholobenko, V. de Waele and S. Mintova, *J. Phys. Chem. C*, 2016, acs.jpcc.6b08045.
 - 88 K.-L. Wong, A. Souici, V. De Waele, M. Mostafavi, T. H. Metzger and S. Mintova, *Langmuir*, 2010, **26**, 4459–64.
 - 89 M. Zahmakiran, F. Durap and S. Özkar, *Int. J. Hydrogen Energy*, 2010, **35**, 187–197.
 - 90 V. De Waele, J. Kecht, Z. Tahri, M. Mostafavi, T. Bein and S. Mintova, *Sensors Actuators B Chem.*, 2007, **126**, 338–343.
 - 91 J. Kecht, Z. Tahri, V. De Waele, M. Mostafavi, S. Mintova and T. Bein, *Chem. Mater.*, 2006, **18**, 3373–3380.
 - 92 M. Severance and P. K. Dutta, *J. Phys. Chem. C*, 2014, **118**, 28580–28591.
 - 93 D. Farrusseng and A. Tuel, *New J. Chem.*, 2016.

- 94 F. Zaera, *Chem. Soc. Rev.*, 2013, **2**, 2746–2762.
- 95 G. Evano, N. Blanchard and M. Toumi, *Chem. Rev.*, 2008, **108**, 3054–3131.
- 96 Y. Lu and W. Chen, *Chem. Soc. Rev.*, 2012, **41**, 3594–623.
- 97 N. Cioffi, N. Ditaranto, L. Torsi and L. Sabbatini, *Approaches to synthesis and characterization of spherical and anisotropic copper nanomaterials*, 2009.
- 98 P. Christian, F. Von Der Kammer, M. Baalousha and T. Hofmann, *Ecotoxicology*, 2008, **17**, 326–343.
- 99 Y. Xia and N. J. Halas, *MRS Bull.*, 2011, **30**, 338–348.
- 100 R. V. Kumar, Y. Mastai, Y. Diamant and a. Gedanken, *J. Mater. Chem.*, 2001, **11**, 1209–1213.
- 101 J. Moghimi-Rad, F. Zabihi, I. Hadi, S. Ebrahimi, T. D. Isfahani and J. Sabbaghzadeh, *J. Mater. Sci.*, 2010, **45**, 3804–3811.
- 102 M. Veerapandian, R. Subbiah, G. S. Lim, S. H. Park, K. Yun and M. H. Lee, *Langmuir*, 2011, **27**, 8934–8942.
- 103 B. K. Park, S. Jeong, D. Kim, J. Moon, S. Lim and J. S. Kim, *J. Colloid Interface Sci.*, 2007, **311**, 417–424.
- 104 M. Blosi, S. Albonetti, M. Dondi, C. Martelli and G. Baldi, *J. Nanoparticle Res.*, 2011, **13**, 127–138.
- 105 S. S. Jushi, S. F. Patil, V. Iyer and S. Mahumuni, *NanoStructured Mater.*, 1998, **10**, 1135–1144.
- 106 J. Ryu, H.-S. Kim and H. T. Hahn, *J. Electron. Mater.*, 2011, **40**, 42–50.
- 107 I. Lisiecki and M. P. Pileni, *J. Am. Chem. Soc.*, 1993, **115**, 3887–3896.
- 108 M. P. Pileni, B. W. Ninham, T. Gulik-Krzywicki, J. Tanori, I. Lisiecki and a Filankembo, *Adv. Mater.*, 1999, **11**, 1358–1362.
- 109 Y. G. Guo, J. S. Hu and L. J. Wan, *Adv. Mater.*, 2008, **20**, 2878–2887.
- 110 G.-R. Li, H. Xu, X.-F. Lu, J.-X. Feng, Y.-X. Tong and C.-Y. Su, *Nanoscale*, 2013, 1–35.
- 111 A. S. Arico, P. Bruce, B. Scrosati and J.-M. Arascon, *Nature*, 2005, **4**, 366–377.
- 112 T. M. D. Dang, T. T. T. Le, E. Fribourg-Blanc and M. C. Dang, *Adv. Nat. Sci. Nanosci. Nanotechnol.*, 2011, **2**, 15009.
- 113 D. Deng, Y. Jin, Y. Cheng, T. Qi and F. Xiao, 2013.
- 114 Y. Kobayashi, S. Ishida, K. Ihara, Y. Yasuda, T. Morita and S. Yamada, *Colloid Polym. Sci.*, 2009, **287**, 877–880.
- 115 S. Mallick, S. Sharma, M. Banerjee, S. S. Ghosh, A. Chattopadhyay and A. Paul, *ACS Appl. Mater. Interfaces*, 2012, **4**, 1313–1323.
- 116 J. E. Mondloch, E. Bayram and R. G. Finke, *J. Mol. Catal. A Chem.*, 2012, **355**, 1–38.
- 117 A. Souici, K.-L. Wong, V. De Waele, J. L. Marignier, T. H. Metzger, N. Keghouche, S. Mintova and M. Mostafavi, *J. Phys. Chem. C*, 2014, **118**, 6324–6334.
- 118 S. a. Anderson, S. Manthata and T. W. Root, *Appl. Catal. A Gen.*, 2005, **280**, 117–124.
- 119 W. X. Zhang, H. Yahiro, N. Mizuno, J. Izumi and M. Iwamoto, *Langmuir*, 1993, **9**, 2337–2343.
- 120 M. Iwamoto, *Stud. Surf. Sci. Catal.*, 1991, 327–334.
- 121 C. Torre-Abreu, C. Henriques, F. . Ribeiro, G. Delahay and M. . Ribeiro, *Catal. Today*, 1999, **54**, 407–418.
- 122 N. V. Beznis, B. M. Weckhuysen and J. H. Bitter, *Catal. Letters*, 2010, **138**, 14–22.
- 123 G. D. Pirngruber, *Ordered Porous Solids*, 2009, 749–771.
- 124 F. Márquez, a. E. Palomares, F. Rey and a. Corma, *J. Mater. Chem.*, 2001, **11**, 1675–1680.
- 125 S. Chassaing, A. Sani Souna Sido, A. Alix, M. Kumarraja, P. Pale and J. Sommer, *Chem. - A Eur. J.*, 2008, **14**, 6713–6721.

- 126 W. Zhang, J. Xie, W. Hou, Y. Liu, Y. Zhou and J. Wang, 2016.
- 127 Z. Tahri, F. Luche, I. Yordanov, O. Poizat, A. Moissette, V. Valtchev, S. Mintova, M. Mostafavi and V. De Waele, *Res. Chem. Intermed.*, 2009, **35**, 379–388.
- 128 M. Zaarour, M. El Roz, B. Dong, R. Retoux, R. Aad, J. Cardin, C. Dufour, F. Goubilleau, J.-P. Gilson and S. Mintova, *Langmuir*, 2014, **30**, 6250–6.
- 129 B. Dong, R. Retoux, V. de Waele, S. G. Chiodo, T. Mineva, J. Cardin and S. Mintova, *Microporous Mesoporous Mater.*, 2017.
- 130 R. Bartolomeu, R. Bértolo, S. Casale, A. Fernandes, C. Henriques, P. Da Costa and F. Ribeiro, *Microporous Mesoporous Mater.*, 2013, **169**, 137–147.
- 131 T. Subramanian and K. Pitchumani, *Catal. Sci. Technol.*, 2012, **2**, 296.
- 132 A. N. Pestryakov, V. P. Petranovskii, A. Kryazhov, O. Ozhereliev, N. Pfänder and A. Knop-Gericke, *Chem. Phys. Lett.*, 2004, **385**, 173–176.
- 133 A. Seidel, J. Loos and B. Boddenberg, *J. Mater. Chem.*, 1999, **9**, 2495–2498.
- 134 L. Lakiss, J. Kecht, V. de Waele and S. Mintova, *Superlattices Microstruct.*, 2008, **44**, 617–625.
- 135 Y. Zeng, H. Walker and Q. Zhu, *J. Hazard. Mater.*, 2016, **324**, 605–616.
- 136 K. T. Højholt, A. B. Laursen, S. Kegnæs and C. H. Christensen, *Top. Catal.*, 2011, **54**, 1026–1033.
- 137 T. Otto, J. M. Ramallo-López, L. J. Giovanetti, F. G. Requejo, S. I. Zones and E. Iglesia, *J. Catal.*, 2016, **342**, 125–137.
- 138 I. Yordanov and R. Knoerr, *J. ...*, 2010, 20974–20982.
- 139 X. Zou, K.-L. Wong, S. Thomas, T. H. Metzger, V. Valtchev and S. Mintova, *Catal. Today*, 2011, **168**, 140–146.
- 140 M. Rivallan, I. Yordanov, S. Thomas, C. Lancelot, S. Mintova and F. Thibault-Starzyk, *ChemCatChem*, 2010, **2**, 1074–1078.
- 141 M. Moliner, J. E. Gabay, C. E. Kliewer, R. T. Carr, J. Guzman, G. L. Casty, P. Serna and A. Corma, *J. Am. Chem. Soc.*, 2016, **354**, jacs.6b10169.
- 142 J. Choi, S. Chan, G. Yip, H. Joo, H. Yang and F. K. Ko, *Water Res.*, 2016, **101**, 46–54.
- 143 M. Zahmakiran, S. Akbayrak, T. Kodaira and S. Ozkar, *Dalt. Trans.*, 2010, **39**, 7521–7527.
- 144 D. Laprune, C. Theodoridi, A. Tuel, D. Farrusseng and F. C. Meunier, *Appl. Catal. B Environ.*, 2017, **204**, 515–524.
- 145 X. Zou, J.-M. Goupil, S. Thomas, F. Zhang, G. Zhu, V. Valtchev and S. Mintova, *J. Phys. Chem. C*, 2012, **116**, 16593–16600.
- 146 Y. Lee, J.-R. Choi, K. J. Lee, N. E. Stott and D. Kim, *Nanotechnology*, 2008, **19**, 415604.
- 147 M. Kaya, M. Zahmakiran, S. Özkar and M. Volkan, *ACS Appl. Mater. Interfaces*, 2012, **4**, 3866–3873.
- 148 A. P. Ingle, N. Duran and M. Rai, *Appl. Microbiol. Biotechnol.*, 2014, **98**, 1001–1009.
- 149 X. Hu, J. Li and J. Wang, *ECS Electrochem. Lett.*, 2014, **3**, D13–D15.
- 150 J. Ramyadevi, K. Jeyasubramanian, A. Marikani, G. Rajakumar and A. A. Rahuman, *Mater. Lett.*, 2012, **71**, 114–116.
- 151 T. Tsoncheva, A. Gallo, I. Spassova, M. Dimitrov, I. Genova, M. Marelli, M. Khristova, G. Atanasova, D. Kovacheva and V. Dal Santo, *Appl. Catal. A Gen.*, 2013, **464–465**, 243–252.
- 152 M. Vallet-Regí, F. Balas and D. Arcos, *Angew. Chemie - Int. Ed.*, 2007, **46**, 7548–7558.
- 153 N. T. K. Thanh, N. Maclean and S. Mahiddine, *Chem. Rev.*, 2014, **114**, 7610–7630.
- 154 V. LaMer and R. Dinegar, *J. Am. Chem. ...*, 1950, **72**, 4847–4854.
- 155 V. K. La Mer, *Ind. Eng. Chem.*, 1952, **44**, 1270–1277.

- 156 S. T. Gentry, S. F. Kendra and M. W. Bezpalko, *J. Phys. Chem. C*, 2011, **115**, 12736–12741.
- 157 M. A. Watzky and R. G. Finke, *Chem. Mater.*, 1997, **9**, 3083–3095.
- 158 M. Hözl, S. Mintova and T. Bein, *Stud. Surf. Sci. Catal.*, 2005, **158**, 11–18.
- 159 K. Norrman, A. Ghanbari-Siahkali and N. B. Larsen, *Annu. Reports Sect. 'C' (Physical Chem.)*, 2005, **101**, 174.
- 160 D. W. Schubert and T. Dunkel, *Mater. Res. Innov.*, 2003, **7**, 314–321.
- 161 2016.
- 162 G. Perego, *Catal. Today*, 1998, **41**, 251–259.
- 163 A. W. Chester and E. G. Derouane, *Zeolite characterization and catalysis: A tutorial*, 2010.
- 164 H. van Bekkum, E. M. Flanigen, P. A. Jacobs and J. C. Jansen, *Introduction to Zeolite Science and Practice-2nd Revised Edition*, Elsevier, 2nd edn., 2001.
- 165 M. Che and J. C. Védrine, *Characterization of Solid Materials and Heterogeneous Catalysts - From Structure to Surface Reactivity*, Wiley-VCH Verlag GmbH & Co. KGaA., 2012.
- 166 G. Pál-Borbély, 2005, **65**, 147–152.
- 167 E. Kissa, *Dispersions: characterization, testing, and measurement*, CRC Press, New York, 1999.
- 168 F. Rouessac and A. Rouessac, *Chemical Analysis: Modern Instrumentation Methods and Techniques*, 2007.
- 169 G. Bergeret and P. Gallezot, *Heterog. Katalyse*, 2002, 738–765.
- 170 D. B. Williams and C. B. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*, 2009, vol. 1–4.
- 171 W. Wan, C. Xiao and X. Zou, *Mesoporous Zeolites Prep. Charact. Appl.*, 2015, 425–460.
- 172 S. Kaliaguine, 1996, vol. 102, pp. 191–230.
- 173 M. Stoecker, *Microporous Mater.*, 1996, **6**, 235–257.
- 174 H. Robson, *Verified synthesis of material - 2nd revised edition*, 2001.
- 175 J. Klinowski, *Anal. Chim. Acta*, 1993, **283**, 929–965.
- 176 R. a. Schoonheydt, *Chem. Soc. Rev.*, 2010, **39**, 5051.
- 177 R. F. Howe, in *Recent Advances and New Horizons in Zeolite Science and Technology*, 1995, vol. 102, pp. 97–139.
- 178 A. Vimont, F. Thibault-Starzyk and M. Daturi, *Chem. Soc. Rev.*, 2010, **39**, 4928–4950.
- 179 F. Zaera, *Chem. Soc. Rev.*, 2014, **43**, 7624–7663.
- 180 S. Thomas, P. Bazin, L. Lakiss, V. De Waele and S. Mintova, *Langmuir*, 2011, **27**, 14689–14695.

Chapter 1

Formation of copper nanoparticles in LTL nanosized zeolite: kinetic study

Introduction

In the past decades, metal and semiconductor nanoparticles with sizes in the range of 1–100 nm have attracted significant attention due to their unique properties, such as photoluminescence, electrochemical and catalytic characteristics.^{1–6} Their properties differ from those of single atoms or bulk metals, which is a consequence of their size and high number of sites available on their surface. It was reported that the catalytic activity of metal nanoparticles (Ag, Au, Cu, Pt, etc.) is increasing with the decrease of their size and that the most active catalysts were those for which the particles are below 5 nm.⁴ However, the small metallic nanoparticles demonstrate low thermal stability and a tendency to sinter under harsh reaction conditions, thereby limiting their application at a large scale. For these reasons, development of effective methods for controlled preparation and stabilization of small metal nanoparticles in order to obtain desirable properties remains one of the most important issues.^{1–6} Substantial progress has been achieved in the synthesis of silver and gold nanomaterials.^{7,8} In this regard, copper nanoparticles (Cu NPs) with controlled size and shape are good alternative material for catalysis, production of conductive inks etc., because of their high conductivity, catalytic properties and much lower cost.⁹ Indeed, supported copper catalysts have been utilized successfully in a wide range of reactions, including selective catalytic reduction of NO_x and SO₂,^{10,11} synthesis and decomposition of methanol,^{12–14} direct dimethyl ether synthesis from syngas,^{15,16} dehydrogenation of cyclohexanol¹⁷ and acetone hydrogenation.¹⁸ However, compared to the extensive studies on gold and silver, reports on

copper nanoparticles are still limited, primarily because of relatively low $\text{Cu}^0/\text{Cu}^{+2}$ redox potential (+0.34 V), which causes spontaneous oxidation at ambient conditions.^{3,9,19} It has been reported that aggregation and oxidation of Cu NPs can be avoided by using various protecting agents, such as polymers, organic ligands or porous materials.²⁰

Porous materials and, in particular, zeolites are promising hosts (matrix) for stabilization metal nanoparticles. Particle size and distribution of metals are controlled by steric restrictions originating from the zeolite topology; the regular pore systems of zeolites provides the defined locations.²¹ Besides the protection of nanoparticles against the aggregation, these materials allow free access of reactants and products to the metal surface. Additionally, the zeolite structure imposes shape selectivity by excluding molecules that are too bulky to diffuse in to the channels.²² However, encapsulated nanoparticles are often hardly accessible by reactants due to diffusion limitations in sub-nanometer channels.²³ Recent developments in the synthesis of nanosized zeolites offer materials in which the mean diffusion path is considerably low. Indeed, the combination of the transport properties within the porous framework of nanosized zeolite with the chemical reactivity of the metal nanoparticles is a promising way to the development of advanced materials for catalysis and new applications.²⁴

Chemical reduction of metal ions (copper, platinum, palladium, etc.) confined in the zeolite host, is the most favorable, because of its simplicity and cost effectiveness. It usually involves the reduction of metal salts in some type of solvent and separation of the reducing agent. It gives particles with various size, morphology, and stability by tailoring the conditions of the reduction process including the time of the reduction, the nature of reducing agent, pH of reaction media, and temperature.²⁵ Accordingly, it requires careful consideration of the reaction conditions, and a comprehensive study of the formation mechanism, as the

reduction of the metal can lead to its migration to the external surface of the matrix, and even destruction of the zeolite crystal structure.²⁶

In this work, we report a facile preparation method for copper nanoparticles, confined in the LTL type nanosized zeolite, using chemical reduction under controlled conditions. The LTL type zeolite was selected due to its one-dimensional pore system that is expected to provide confined medium for narrow size distribution of copper nanoparticles. The copper cations were introduced in zeolite nanocrystals via ion exchange post synthesis treatment directly in the suspensions. Subsequently, the copper ions were treated with three reducing agents (hydrazine monohydrate, triethylamine and sodium borohydride), among all the hydrazine was found to be the most effective. Further, the evolution of copper species and formation of copper nanoparticle (Cu⁰ NPs) was followed by *in situ* UV-vis absorption spectroscopy and *ex situ* wide-angle powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and nitrogen adsorption/desorption analysis.

Experimental

Materials

Aluminum hydroxide (reagent grade, Sigma-Aldrich), LUDOX[®] SM 30 colloidal silica (30 wt. % suspension in H₂O, Sigma-Aldrich), potassium hydroxide (ACS reagent, ≥85%, pellets, Sigma-Aldrich), copper(II) nitrate trihydrate (puriss. p.a., 99-104%, Sigma-Aldrich), ammonium hydroxide solution (28%, Prolabo), hydrazine monohydrate (64-65 %, reagent grade, 98%, Prolabo), triethylamine (≥99%, Sigma-Aldrich) and sodium borohydride (Fluka), were used as received.

Preparation of copper containing LTL-type zeolite nanocrystals

Zeolite nanocrystals with LTL-type structure were prepared from clear precursor suspensions with the following molar composition: 5 K₂O : 10 SiO₂ : 0.5 Al₂O₃ : 200 H₂O.²⁷ The as-prepared precursor suspensions were aged at room temperature for 24 hours prior to

hydrothermal treatment at 170 °C for 18 hours. After the crystallization process was accomplished, the nanosized zeolite crystals were recovered by multistep centrifugation (20000 rpm, 40 min) and washed with doubly distilled water until pH = 7 - 8. Prior to incorporation of copper, the LTL nanosized crystals were stabilized in water suspension with a solid concentration of 2.5 wt.% (the sample was denoted as parent LTL).

The ion-exchange was performed directly in the colloidal suspensions without preliminary calcination of the LTL zeolite. Samples were prepared by mixing copper nitrate (0.1 M) with zeolite suspensions, giving solutions containing 0.3 mmol Cu⁺²/g zeolite (the sample was named as Cu²⁺-LTL). The ion-exchange process was carried out at room temperature for 2 hours, and then the solutions were purified by multi-step centrifugation to remove the excess of copper ions, and finally redispersed in double distilled water.

Chemical reduction of copper cations in zeolite suspensions

Copper exchanged zeolite suspensions were reduced with the following reducing agents under identical conditions: sodium borohydride, triethylamine and hydrazine. In a typical experiment the Cu⁺²/reductant ratio is fixed at 1/1000 to maintain reducing conditions and to avoid oxidation of copper nanoparticles, so complete reduction of copper cations was expected. During the addition of the reductant, the mixture was kept at room temperature under magnetic stirring and N₂ atmosphere, due to the high sensitivity of the copper to oxygen. Aliquots of samples were removed periodically from the reaction mixture and freeze-dried with or without washing prior to further studies. The sample obtained after reduction will be further denoted as Cu⁰-LTL.

Characterization

The crystalline structure of the samples was studied by using a PANalytical X'Pert Pro diffractometer with Cu K α monochromatized radiation (λ = 1.5418 Å). The samples were

scanned in the range 3-80 ° with a step size of 0.02°. The XRD patterns were fit in PANalytical X'Pert Pro HighScore Plus software using Pawley fit.

The agglomeration and average size of particles in the crystalline product were determined by dynamic light scattering (DLS) performed with a Malvern Zetasizer Nano instrument (scattering angle of 173°, laser wavelength of 632.8 nm, output power of 3 mW).

The thermal stability of the Cu-LTL samples in comparison to parent LTL zeolite was studied by thermo-gravimetric analysis (TG/DTG) using a Setaram TGDSC 111 analyzer; the measurements were carried out with a heating rate of 5 °C·min⁻¹ under a 40 ml·min⁻¹ flow of air from 25 – 800 °C.

The surface and textural properties of the materials were measured by nitrogen sorption. Nitrogen adsorption/desorption isotherms were obtained using a Micrometrics ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 300 °C under vacuum overnight prior to the measurement. The external surface area and micropore volume were estimated by alpha-plot method using Silica-1000 (22.1 m² g⁻¹ assumed) as a reference. The micropore and mesopore size distributions of the samples were extracted from the adsorption branch using the Nonlocal Density Functional Theory (NLDF), and the desorption branch using the Barret-Joyner-Halenda (BJH) algorithm, respectively.

Chemical composition of samples was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian ICP-OES 720-ES. Additionally, the size, the shape and chemical composition of crystals were revealed by high resolution transmission electron microscopy (HRTEM). The distribution of copper cations in the zeolite crystals was investigated by energy dispersive analysis (EDX, element mapping). The HRTEM and EDX studies were performed using a Tecnai G2 30 UT (LaB₆) microscope operated at 300 kV with 0.17 nm point resolution and equipped with a EDAX EDX detector. Besides, the size and distribution of copper particles were studied by high angle annular dark field (HAADF)

scanning transmission electron microscopy (STEM). High angle annular dark field and annular bright field (ABF) – scanning TEM studies were performed using a JEOL ARM200F cold FEG double aberration corrected electron microscope operated at 200 kV and equipped with a large solid-angle centurio EDX detector and Quantum EELS spectrometer. Particles size distribution was calculated from HAADF STEM images using an imageJ processing software.

The evolution of copper species in the zeolite was studied by *in situ* UV-Vis spectroscopy using a Varian Cary 4000 Spectrophotometer. The measurements were performed in a quartz cuvette (0.5 cm) closed with the septic stopper under N₂ atmosphere. The data acquisition was performed in a cycle mode with a step of 10 min between the spectra.

Results and discussion

Preparation and characterization of nanosized zeolite crystals

X-ray diffraction patterns of parent and ion exchanged LTL (Cu²⁺-LTL) zeolite samples are shown in Figure 1A. Only the Bragg peaks corresponding to pure crystalline LTL zeolite are present in the XRD. The changes of the unit cell parameters of the parent LTL and copper containing samples were studied using Pawley fit (the Pawley fit offers almost all possibilities of a Rietveld refinement, but it does not require crystal structure data). This methodology allows to generate peak positions from a unit cell and symmetry information.²⁸ The simulated XRD patterns, the difference between calculated and experimental data, and the agreement indices are presented in the Figure 2 and Table 2.

The unit cell parameters were refined; parent LTL zeolite: $a = b = 18.37299$ and $c = 7.540921$ and Cu²⁺-LTL zeolite: $a = b = 18.374080$ and $c = 7.544786$. As can be seen, the copper incorporation causes the expansion of the unit cell, probably due to higher affinity of copper cations occluded in the channels to water.²⁹ Further discussion will be presented in Chapter 4. No copper aluminates are detected in these XRD patterns that is in agreement with previous

reports; indeed, the formation of copper aluminates requires the annealing at 900 °C.^{30–33} The broadening of the diffraction peaks in Figure 1A suggests that the size of the LTL crystals is in nanometer range. Their size distribution and morphology before and after incorporation of copper cations were investigated by HRTEM.

HRTEM images (Figure 1B) show rectangular crystals (10 – 20 nm) and with well-defined edges; these nanocrystals tend to align and aggregate to bigger entities (50-70 nm). This can be explained with the several steps of post synthesis treatment (ion-exchange and purification) of the suspensions, leading to change of the alkalinity of the suspensions.

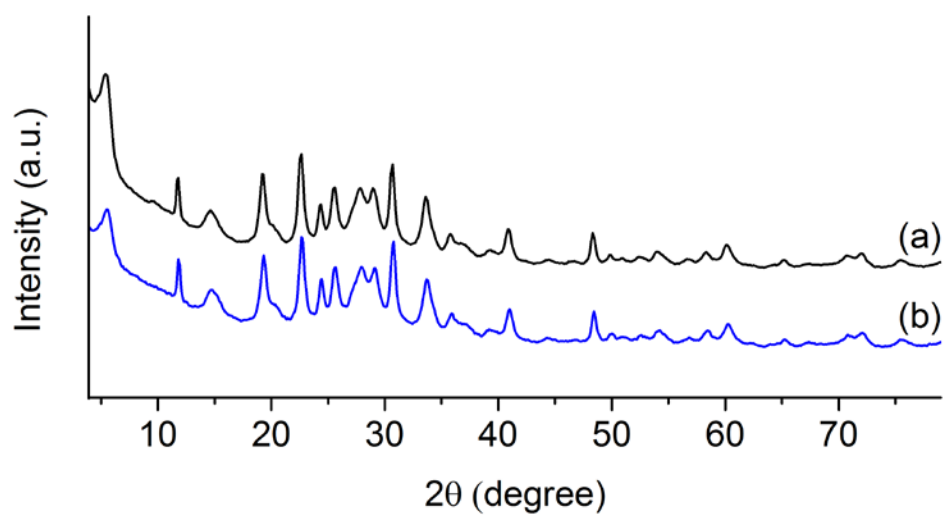
The chemical composition of the samples separated from the suspensions before and after copper incorporation was determined by EDX and ICP-OES techniques. The results are presented in Table 1.

Table 1 Elemental composition of parent LTL and Cu²⁺-LTL zeolite samples measured by ICP-OES and EDX.

Sample	Si/Al		K/Al		Cu/Al	
	ICP	EDX	ICP	EDX	ICP	EDX
Parent LTL	2.85	2.37	2.05	0.88	/	/
Cu ²⁺ -LTL	2.83	2.39	1.36	0.81	0.06	0.10

The results show that potassium was only partially exchanged by copper cations, and this is explained by the stability of potassium cations (K⁺) occluded in the cancrinite cages, that cannot be exchanged by other cations.³⁴ Moreover, the most common ion exchange Cu²⁺ complex [Cu(H₂O)₆]²⁺ in copper solutions is too large to diffuse through the 6MR's.³⁵ The results indicate a copper loading of 1.2 wt. %, that corresponds to ~0.6 Cu²⁺ ions per unit cell.

(A)



(B)

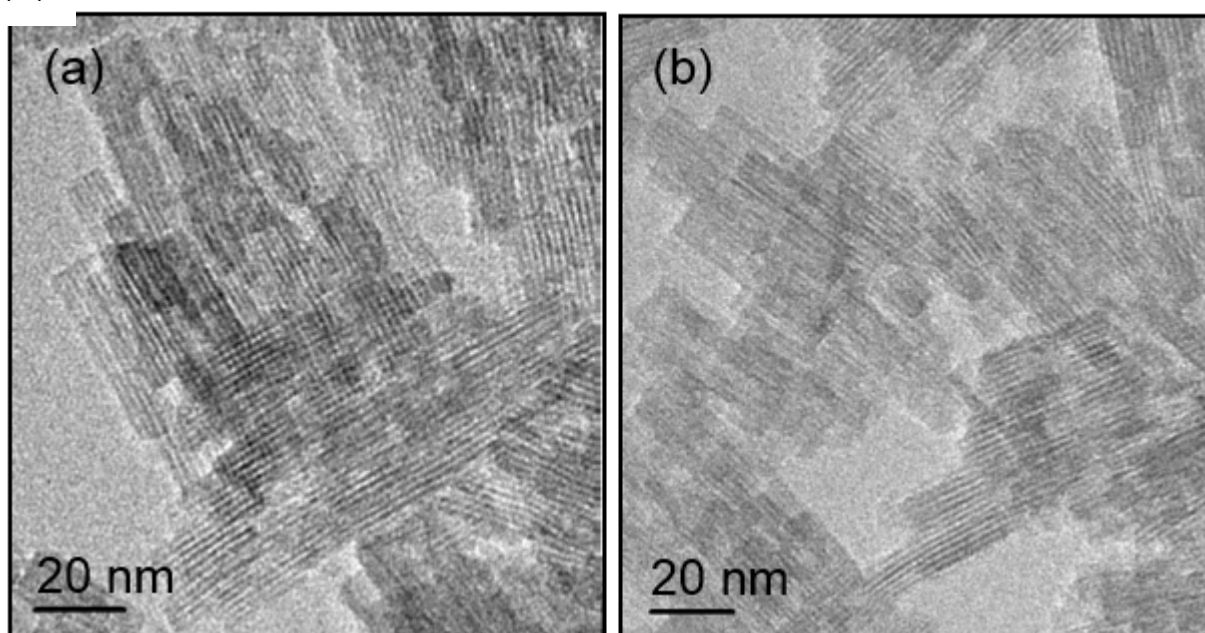
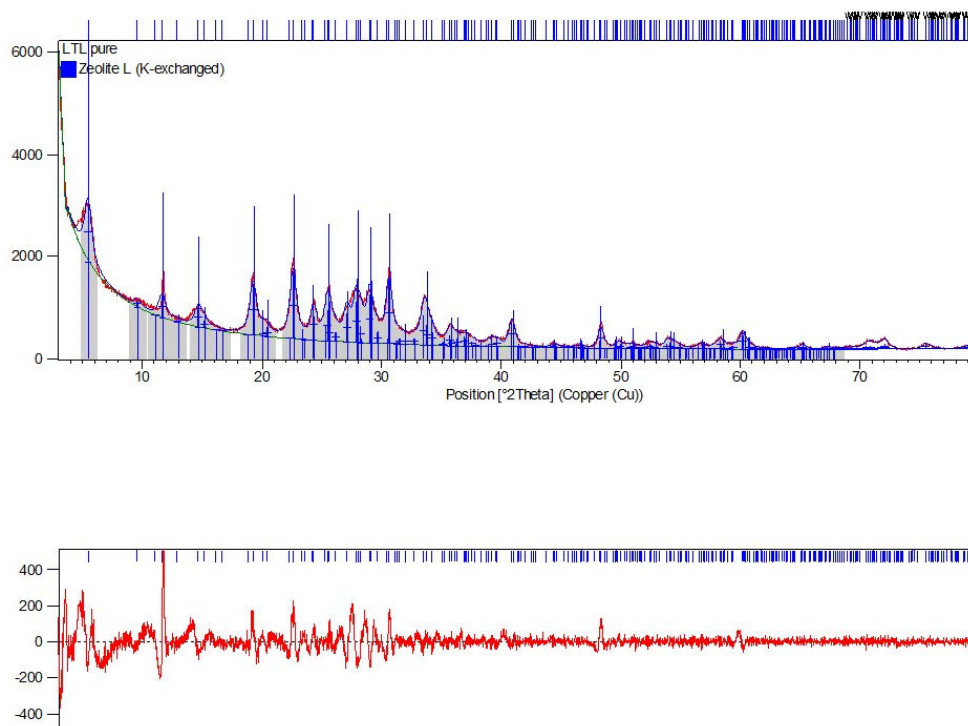


Figure 1 (A) XRD patterns of (a) parent LTL and (b) Cu^{2+} -LTL samples. (B) TEM images of (a) parent LTL and (b) Cu^{2+} -LTL samples

(A)



(B)

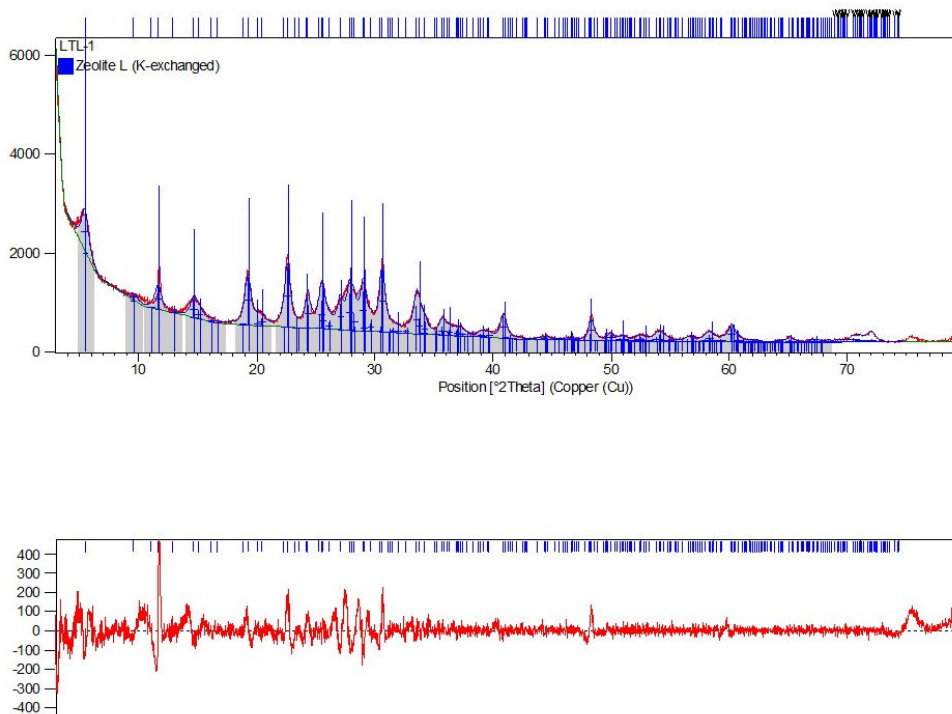


Figure 2 Pawley fit of the XRD patterns and difference diagram between calculated and experimental data of (A) parent LTL and (B) Cu⁰-LTL; a unit cell is used to generate the initial peak list, as a reference pattern the Zeolite LTL (K-exchanged) (No. 98-003-5486) was used

Table 2 Agreement indices for the Pawley fit of the parent LTL and Cu⁰-LTL

Agreement Indices	Parent LTL	Cu ⁰ -LTL
R expected	3.7244	3.6959
R profile	4.3126	4.1496
Weighted R profile	5.6025	5.8898
D-statistics	0.2734	0.3293
Goodness of Fit	1.5043	1.5936

In addition, the EDX-TEM mapping of the Cu²⁺-LTL sample is presented in Figure 3. The homogeneous distribution of copper across the LTL nanosized zeolite is clearly observed, which is required to obtain copper nanoparticles with narrow size distribution.

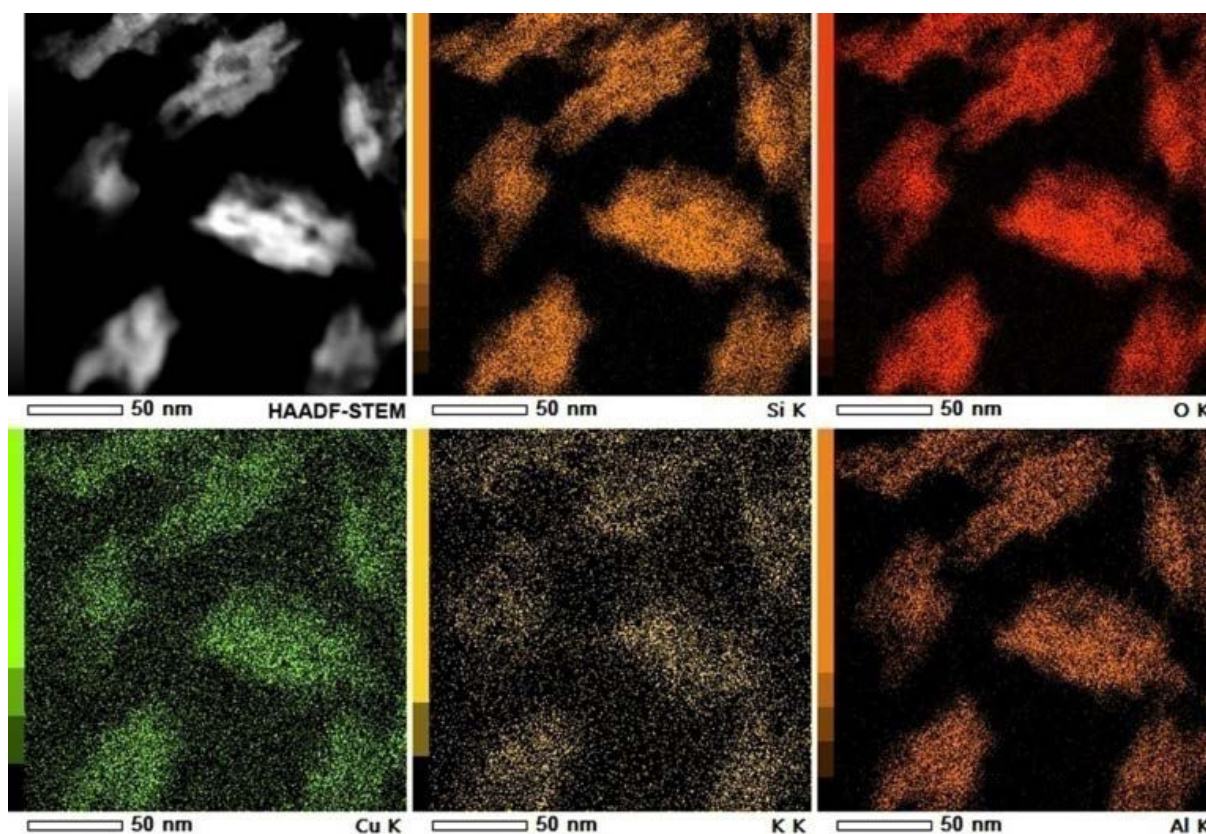


Figure 3 Qualitative elemental analysis of Cu²⁺-LTL sample by EDX-TEM mapping.

Kinetics of formation of Cu nanoparticles in LTL zeolite suspensions via chemical reduction

The kinetics of formation of copper nanoparticles in the Cu^{2+} -LTL zeolite suspensions (concentration of 2.5 wt.%) was studied (see Experimental section). Initially, the steady-state UV-Vis spectra of the three samples prepared with different reducing agents were collected (Figure 4). Based on the UV-vis spectra, the properties of the metal nanoparticles were evaluated; it is known that the surface plasmon polarization resonance (SPP) of nanoparticles is influenced by the size, shape, interparticle interactions, free electron density and surrounding medium.³⁶ The reduction of copper ions (Cu^{2+}) to metal (Cu^0) nanoparticles in the presence of sodium borohydride occurred rapidly at ambient conditions. The absorption peak at 570 nm (Figure 4a) is attributed to SPP resonance of the metallic copper nanoparticles. The low intensity of the band is explained by the fast formation of black precipitate, indicating the formation of large Cu nanoparticles.³⁷ This result is also confirmed with SEM studies showing cubic nanoparticles with a size of about 170 nm (Figure 5). The reducing agent (NaBH_4) has been used in excess (1/1000). The excess of sodium must have resulted in back-exchange of copper facilitated by the small zeolite crystals and one-dimensional topology of the channels. This would explain the large size of the copper metal particles formed at the external surface of the zeolite crystals and in the solution. Sodium borohydride is a very strong reducing agent, and the reduction occurs much faster than the actual growth of the particles followed by aggregation and coalescence resulting in the formation of bulky copper nanoparticles outside the zeolite matrix.³⁸

The Cu^{2+} -LTL sample treated with triethylamine shows two absorption bands located at 360 nm and 420 nm (Figure 4b); these are charge transfer bands of Cu-O-Cu and O-Cu-O complexes, respectively according to previously reported data.^{19,39} The same bands were assigned to the copper oligomers in polymer and inorganic matrices.^{40–42} Moreover, the same peaks were assigned to Cu^{I} species in the Cu_2O microspheres and nanocrystals.^{4,43,44} The

plasmon band at 570 nm is not observed for this sample. The results suggest that the strong reducing agent (triethylamine) previously applied for synthesis of other nanoparticles (Au and Ag),^{45–47} does not participate in the reduction of Cu^I species to Cu⁰.

The absorption spectrum of Cu²⁺-LTL sample treated with hydrazine demonstrates well defined broad peak centered at 590 nm that appeared after 3 hours of the reduction (Figure 4c), which is a clear indication of the formation of Cu NPs. This suspension is stable and no formation of black precipitate is observed. Hence, the kinetics of Cu⁰ formation in the LTL zeolite suspension treated with hydrazine was studied in further details.

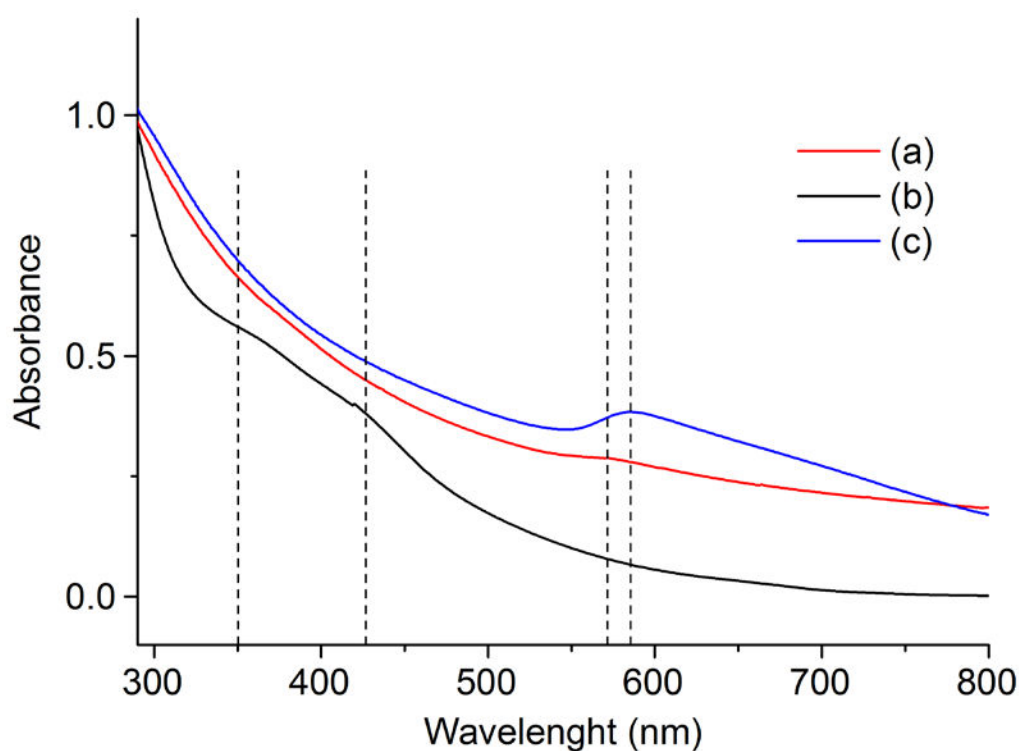


Figure 4 UV-vis spectra of Cu NPs formed in LTL zeolite suspensions under N₂ atmosphere using (a) sodium borohydride, (b) triethylamine and (c) hydrazine as reducing agents

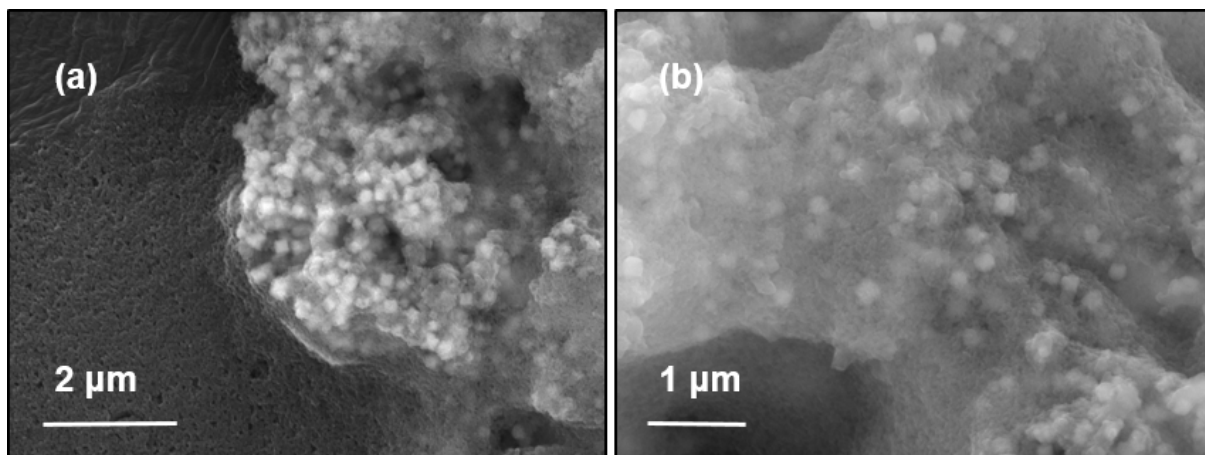


Figure 5 SEM image of Cu²⁺-LTL reduced with Sodium borohydride. Cubic shaped copper nanoparticles on the surface of nanosized LTL crystals are observed

In order to obtain more information about the formation of copper species during the reduction process, the kinetic study was performed at room temperature under nitrogen atmosphere in excess of hydrazine to prevent copper particles oxidation and to avoid the reaction between oxygen and hydrazine.⁴⁸

The exhalation of N₂ bubbles indicates that reduction is proceeding according to the following reaction: $\text{Cu}^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{Cu}^0 + \text{N}_2 + 4\text{H}_2\text{O}$.

The spectra of the reaction mixture were collected after equal intervals of time (10 minutes). The evolution of the UV-vis spectra (200 – 800 nm) of the sample during reduction with hydrazine is presented in Figure 6A. The initial spectrum of the Cu²⁺-LTL sample is featureless. After 180 min, the color of the suspension changes drastically from light blue to reddish, and a broad band at 590 nm arises, that is assigned to the SPP resonance band of metallic copper (Cu⁰). The spectrum looks essentially similar to ones reported in the literature for copper nanoparticles, but the peaks position is slightly “red-shifted”.⁴⁹ This can be explained by increase of optical contrast between the particles (ϵ) and surrounding matrix (ϵ_m), which causes the growth of magnitude and shift to longer wavelengths of the SSP resonance peaks in comparison to nanoparticles in vacuum.^{37,50} In our case the Cu NPs are stabilized in the LTL zeolite crystals (refractive index, RI =1.164) and dispersed in DD water (RI = 1.33 at 20 °C).

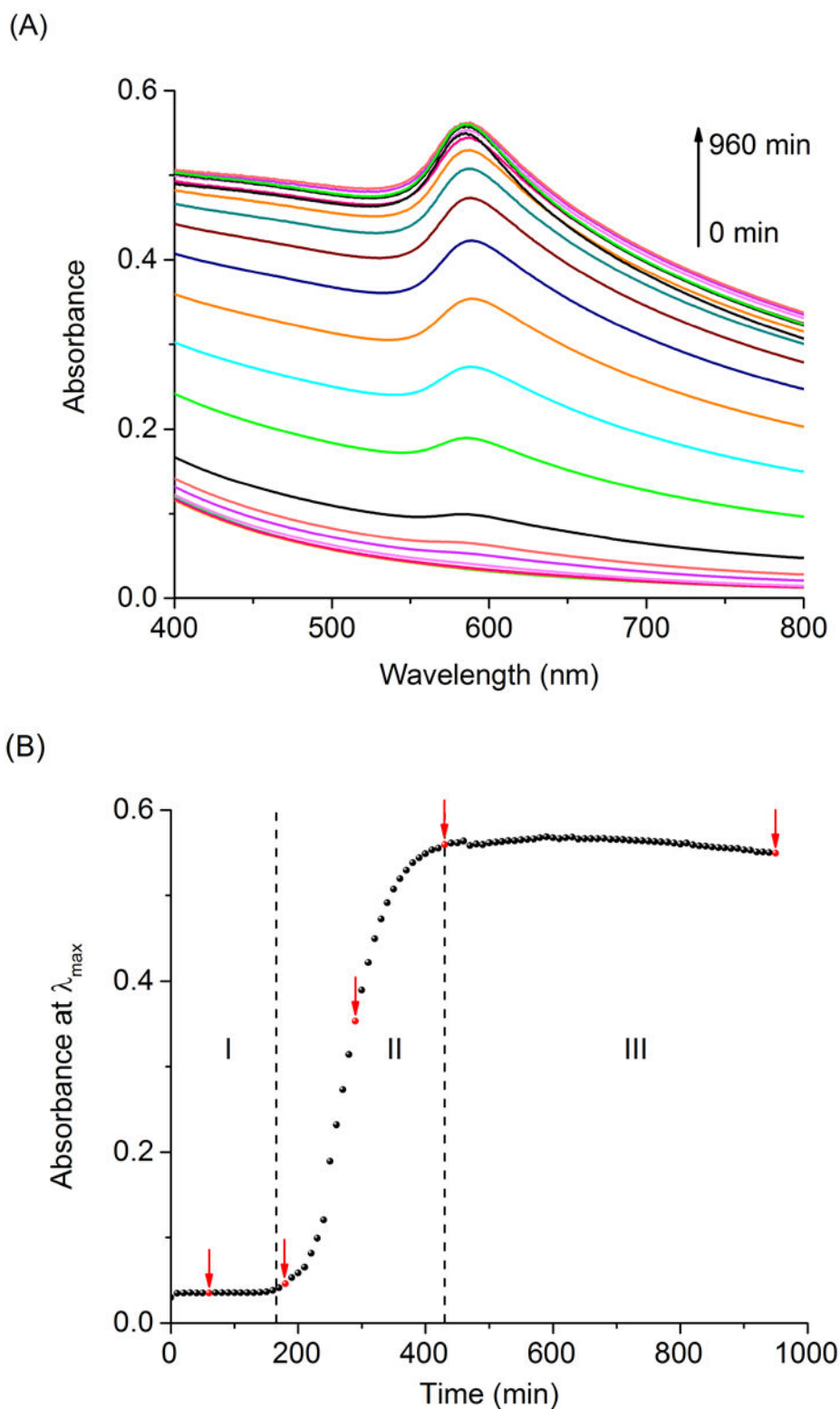


Figure 6 (A) Evolution of extinction spectra of copper containing LTL suspension (solid zeolite concentration of 2.5 wt. %) reduced with hydrazine with time (not all the spectra are shown). (B) Variation of peak intensity at $\lambda_{\text{max}} = 590 \text{ nm}$ in the course of reduction reaction. The dashed vertical lines emphasize the reduction steps (I, II, III). The red arrows and red balls highlight the key times, when the materials were extracted for further characterization

As reduction process proceeds, no obvious change in the peak position and shape during the first 16 h is observed, apart from the peak intensity during 430 min (step I and II); also, no new peaks appeared in the spectra. According to Mie's theory, a single SPP resonance peak is expected for spherical nanoparticles, while particles with anisotropic shape could give two or more SPP resonance peaks depending on their shape.^{49,51,52} It is worth noticing, that after 430 min a slight decrease in the absorbance peak intensity at the same λ_{max} occurs. This might indicate the aggregation of copper nanoparticles located outside the zeolite matrix and their partial sedimentation. However, it is difficult to judge the size and location of the copper particles by UV-vis spectra in this particular case due to the complexity of the surrounding medium and possible migration of the particles from zeolite matrix to the solution followed by aggregation. Therefore, the size of the CuNPs was studied by HRTEM and the results will be discussed further.

Numerous models describing the mechanism of formation of metal nanoparticles are discussed in the literature.^{8,38} The development of the absorption peak at 590 nm for the Cu-LTL sample as a function of time is presented in Figure 6B. The process of formation of Cu NPs could be conditionally divided in three steps. A long induction period (I step) is followed by a rapid growth after 3 hours (II step), then the absorbance reaches maximum after 7 hours and later on slightly decreases (III step). The induction period can be explained by the intermediate formation of Cu^+ species and Cu_n^+ oligomers by the following dismutation reaction: $\text{Cu}^{2+} + \text{Cu}^0 \rightarrow 2\text{Cu}^+$,

since the atomic potential for $E^\circ (\text{Cu}^+/\text{Cu}^0)$ is $-2.7\text{V}_{\text{NHE}}$ (normal hydrogen electrode).¹⁹ However, there is no evidence of these species in the UV-vis spectra.

Assuming the molar extinction coefficient of copper is $2100 \text{ L mol}^{-1} \text{ cm}^{-1}$,⁴² the amount of Cu^0 can be calculated on the basis of the absorption spectra from the Beer-Lambert law. The

concentration of Cu^0 is estimated to be around 0.5 mmol L^{-1} that corresponds to the reduction of about 90 % of initial Cu^{2+} to Cu^0 .

Further, the aliquots of the reaction mixture at each reduction stage, were collected and freeze-dried; the powder samples were stored in a glove box under argon to avoid copper oxidation prior to further studies.

The formation of copper nanoparticles and their influence on the crystallinity of the LTL zeolite matrix were followed by recording the XRD patterns at various times of reduction (Table 3).⁵³

Table 3 Analysis of Bragg peak area of the XRD patterns collected at different key times of the reaction

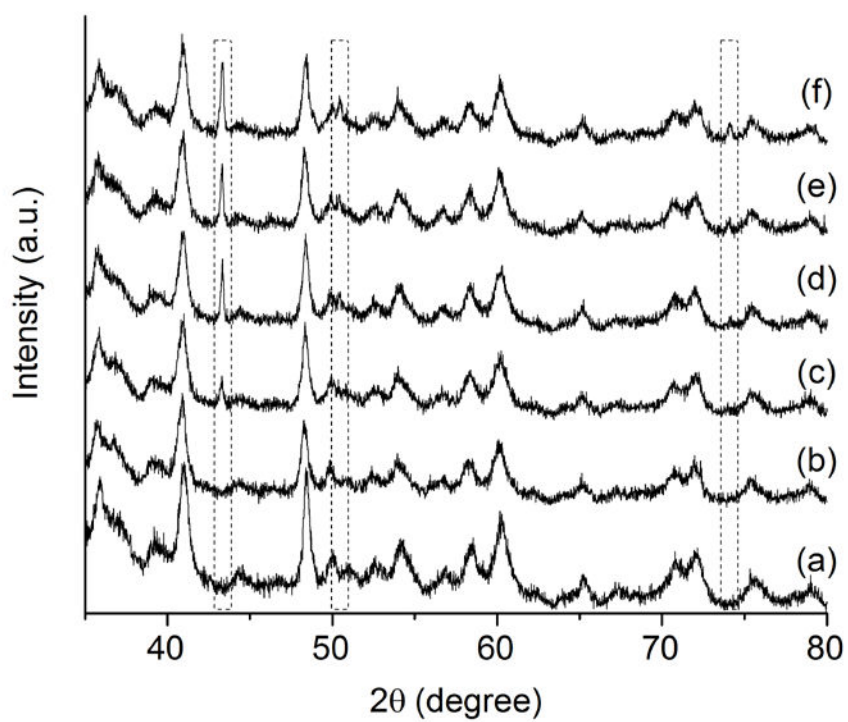
Sample Cu^{2+}-LTL	X_{beg}	X_{end}	Y_{max}	$X(Y_{\text{Max}})$	Peak Area
0 min	42.90	43.70	43.08	43.61	0.04
70 min	42.90	43.70	37.19	43.65	-0.06
190 min	42.90	43.70	140.00	43.29	44.24
280 min	42.90	43.70	263.00	43.33	56.23
430 min	42.90	43.70	258.00	43.31	64.25
960 min	42.90	43.70	309.00	43.33	92.42

$X_{\text{beg}}-X_{\text{end}}$ – peak position

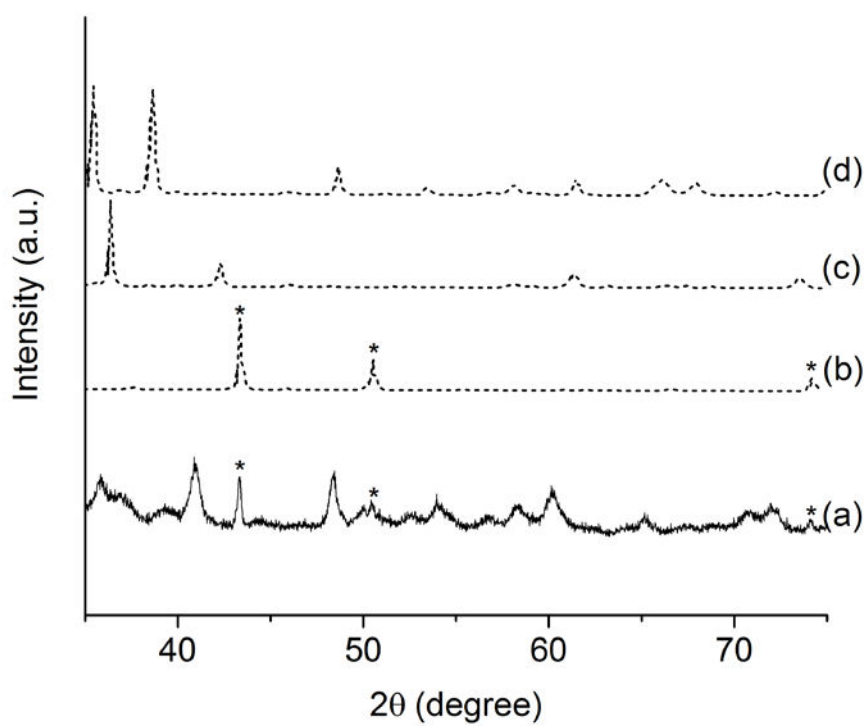
The XRD patterns of the material in the range $35 - 80^\circ 2\theta$ are presented in Figure 7A. During step I (check point 1 at 70 min), no diffraction peaks for Cu^0 are observed. It is known, that pore opening of the LTL zeolite is $7.1-7.4 \text{ \AA}$, and the Van der Waals size of the hydrazine molecule is $3.43 \text{ \AA}$, that permits its diffusion inside the zeolite pores (Figure 8).

Therefore, according to LaMer theory of nanoparticle growth, zero valence Cu^0 is constantly produced in the zeolite voids until the concentration of copper atoms reaches a critical point, and then the Cu atoms would spontaneously condense.^{8,54} When the formed nuclei are too small, their crystalline structure is not defined and therefore the Bragg peaks are not seen.

(A)



(B)



(C)

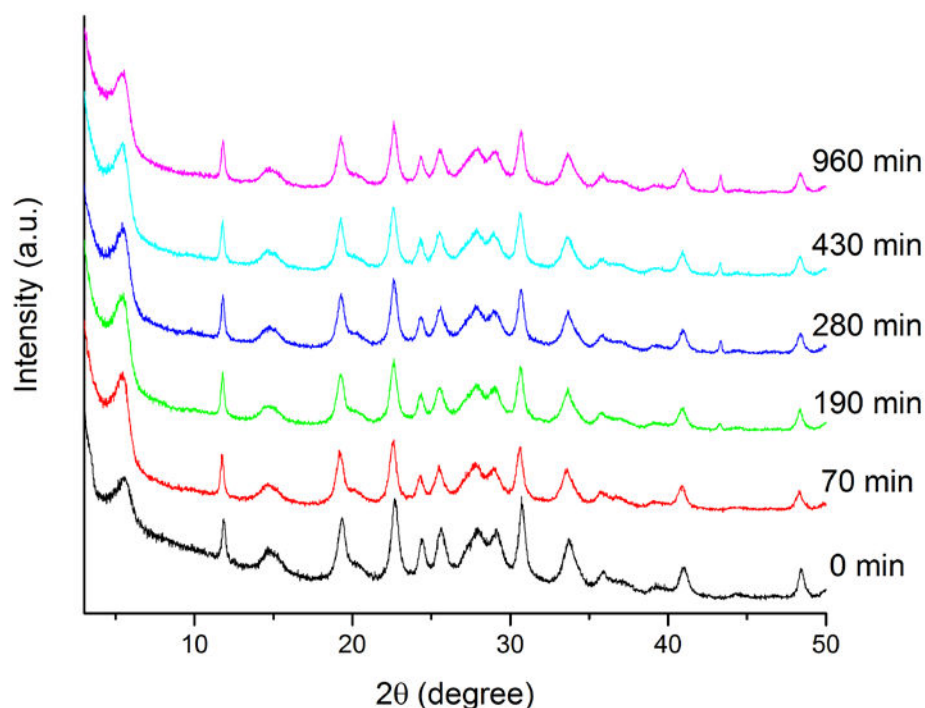
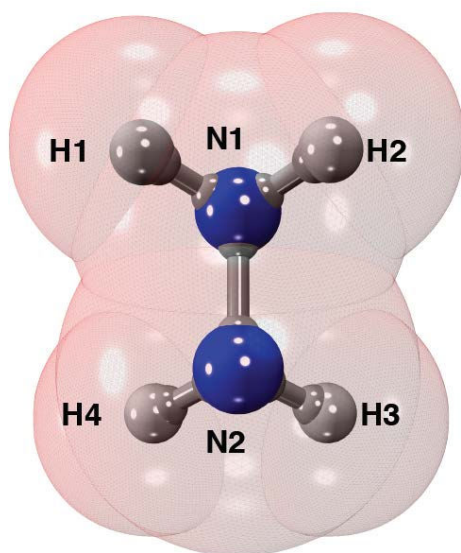


Figure 7 (A) XRD patterns of solid samples isolated during the reduction of copper containing LTL suspension in the range of 35 -80 °2θ after (a) 0 min, (b) 70 min, (c) 190 min, (d) 280 min, (e) 430min and (f) 960min. The characteristic metallic copper peaks at 43.3, 50.4 and 74.2 °2θ are indicated with dashed rectangles. (B) Reference patterns of (a) Cu⁰-LTL after reduction for 960 min, (b) Cu⁰ and (c) Cu₂O and (d) CuO. The asterisk (*) indicate Cu⁰ peaks. No oxides are observed in the sample. (C) XRD patterns of samples at different reaction time in the region 4 - 50 °2θ. The LTL zeolite structure stays intact during the reduction process



Van der Waals surface

Atoms	d, Å
H1-H2	1.62
H1-H3	2.90
H1-H4	2.41
N1-N2	1.44

Atoms	Radii, Å
H	0.53
N	0.56

Figure 8 Van der Waals size of Hydrazine molecule

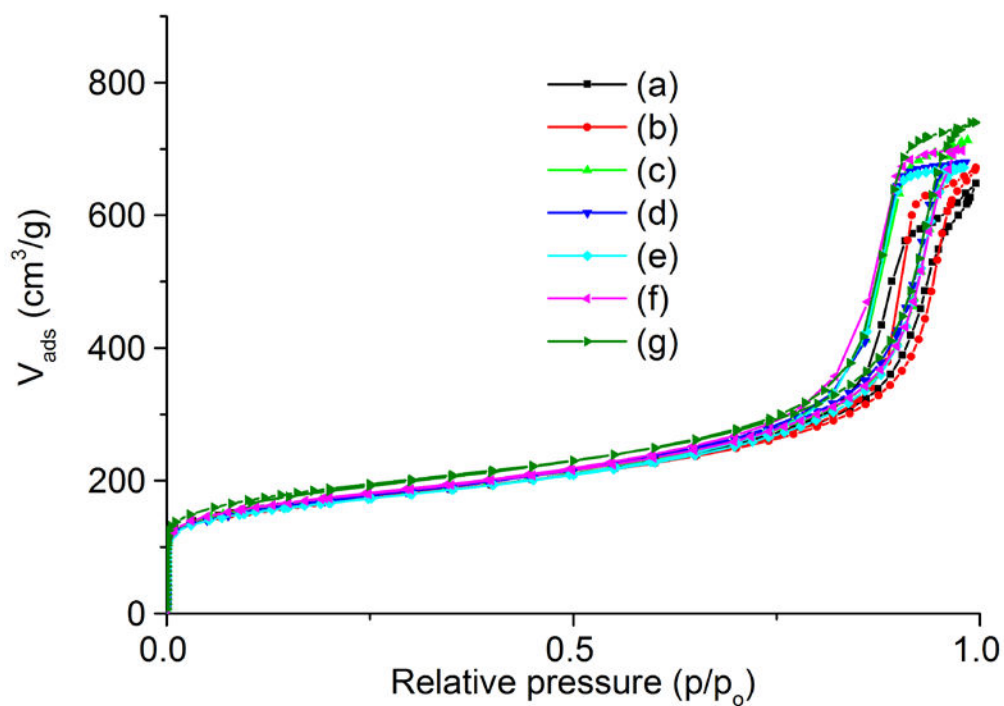
There are three peaks in the XRD pattern attributed to metallic copper nanoparticles: at 43.3 °, which can be readily indexed to the (111) crystalline plane, emphasizing the hexagonal packing of the surface layer atoms; two more weak peaks at 50.3 and 74.2 ° correspond to (200) and (220) crystalline planes, respectively, can be observed.⁵⁵ The latter appear after 3 h (point 2 at $t = 190$ min, step II), indicating some copper nanoparticles are large and stable enough to be detected with XRD. The acceleration of the nanoparticles growth continues up to $t = 430$ min (point 3 $t = 280$ min, point 4 $t = 430$ min, step III), and reaches the maximum and remains constant, thus indicating the steady-state of reduction (point 5 at $t = 960$ min). It should be noted that no copper(I) or copper (II) oxides have been observed in the XRD pattern (Figure 7B). During the reduction process there is no change in signal to noise ratio, confirming that the zeolite structure stays intact (Figure 7C).⁵³

The porosity of the parent LTL and copper containing LTL samples at different reduction stages was monitored *via* low temperature nitrogen sorption (Figure 9A (a – g)). All isotherms are a mixture of type I and type IV, typical for microporous materials, represented by the rapid uptake at low relative pressures followed by nearly horizontal adsorption and desorption branches. The hysteresis loop at high relative pressures appears due to the formation of textural mesopores, which can be explained by the close packing of monodispersed zeolite nanoparticles.⁵⁶ Figure 9B, Figure 9C and Table 4 display the variations in surface area and pore volume of the samples at different reaction steps. As can be seen the BET surface area and the external surface area do not change significantly. The micropore volume (t-plot method was applied) follows the same trend. This confirms the previous observations, that the zeolite structure is stable and no amorphization is observed.

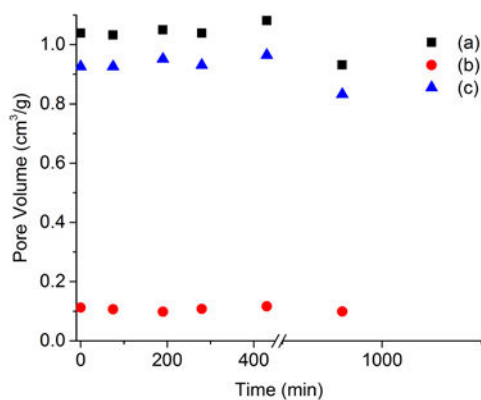
Table 4 The BET surface area (S_{BET}), external surface area (S_{EXT}), and micro- (V_{mic}), meso- (V_{meso}) and total (V_{tot}) pore volumes of samples at different time of reduction with hydrazine

Sample	S_{BET}, $\text{m}^2 \text{g}^{-1}$	S_{EXT}, $\text{m}^2 \text{g}^{-1}$	V_{mic}, $\text{cm}^3 \text{g}^{-1}$	V_{tot}, $\text{cm}^3 \text{g}^{-1}$	V_{mes}, $\text{cm}^3 \text{g}^{-1}$
Parent LTL	571.4	320.7	0.12	1.00	0.88
Cu^{2+}-LTL (0 min)	571.9	339.8	0.11	1.04	0.93
70 min	544.4	343.9	0.11	1.03	0.93
190 min	568.4	378.6	0.10	1.05	0.95
280 min	553.4	345.2	0.11	1.04	0.93
430 min	573.9	349.5	0.12	1.08	0.96
960 min	518.3	327.1	0.10	0.93	0.83

(A)



(B)



(C)

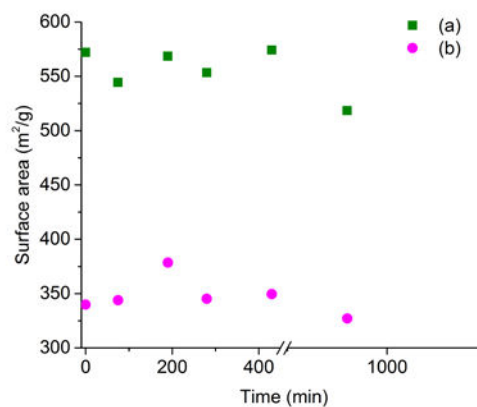


Figure 9 (A) Nitrogen adsorption/desorption isotherms of (a) parent LTL, (b) Cu^{2+} -LTL, and the Cu^{2+} -LTL sample after reduction for (c) 70 min, (d) 190 min, (e) 290 min, (f) 430 min, and (g) 960 min; (B) (a) micropore volume (V_{mic}), (b) mesopore volume (V_{meso}) and (c) total pore volume (V_{total}); (C) (a) BET surface area (S_{BET}) and (b) external surface area (S_{ext}) of copper containing LTL as a function of reduction time

The size and location of Cu NPs in the samples during reduction were studied by HAADF-STEM; the images of the samples at key reaction points with hydrazine are shown in Figure 10. After 70 min no sign for copper nanoparticles is detected (Figure 10a). The copper nanoparticles are identified as the bright spots uniformly distributed in the Cu-LTL sample after 190 min (Figure 10b), which are not found in the previous sample. The Cu NPs show a narrow size distribution in the range of 0.2 – 1.6 nm (mean size of 1 nm, Figure 11A). That is somewhat bigger than the pore opening of the LTL-type zeolite (0.74 nm) and the large cavity diameter (1.07 nm).⁵⁷ However, it was previously found that zeolitic and MOF's structures can be locally distorted by the metal particles with the size bigger than the cages while still preserving the original crystalline structure.^{58,59} Bright field (BF) TEM images also show part of the Cu particles oriented along the LTL-crystals channels, giving the idea of their location inside the zeolite. Nevertheless, the exact position of particles cannot be elucidated from the BF alone, because of the two-dimensional nature of the image.⁶⁰ On the other hand, nitrogen adsorption/desorption data demonstrate, that there is no noticeable blockade of the zeolite pores with the growing copper nanoparticles. This phenomenon can be explained by low concentration of copper in the sample (1.2 wt. %), so that the Cu NPs formed do not affect the texture of the entire material. As seen from the XRD and N₂ sorption measurements in combination with the TEM, one can conclude that the copper nanoparticles are both inside the channels and on the surface of the zeolite crystals. After 280 min reduction (Figure 10c), more copper particles in the sample are observed. One can see, that there are no copper nanoparticles with a size smaller than 0.4 nm, at the same time there are particles with a diameter of 2.2 nm (this fraction of Cu NPs is situated on the surface of the zeolite crystals, Figure 11B). It was reported earlier, that a dissolution of small particles (radius < 0.5 nm) at temperatures lower than 200 °C is very unlikely. Since the reaction here is performed at room temperature, the aggregation or coalescence of copper nanoparticles

caused by poor colloidal stability is a much more probable process than Ostwald ripening due to particles dissolution.³⁸ It was shown before, that in hydrated form metal nanoparticles are extremely mobile.²⁶ Consequently, the Cu NPs confined in the pores of the LTL zeolite can migrate to the surface, initiating further increase of their size. The images taken from the sample after 430 min of reduction (Figure 7d) display large copper particles (100 nm) on the surface of aggregated zeolite crystals. Small copper NPs resemble those observed in the beginning of the process are still presented within the host, but their amount is notably lower, and the distribution is no longer homogeneous along the zeolite crystals (Figure 10d'). After 960 min of reduction (Figure 7e), there are no more small copper nanoparticles. Migration and aggregation of Cu NPs from the channels of the LTL zeolite led to the generation of large copper particles.

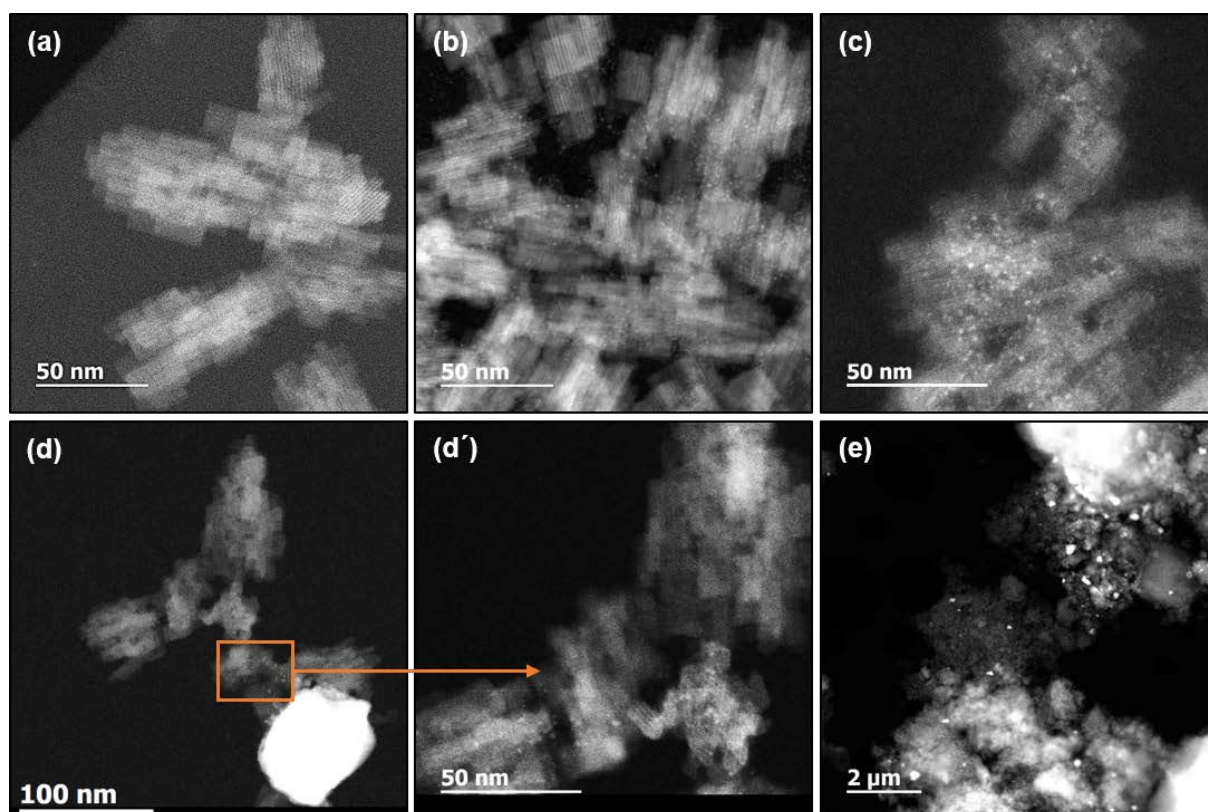
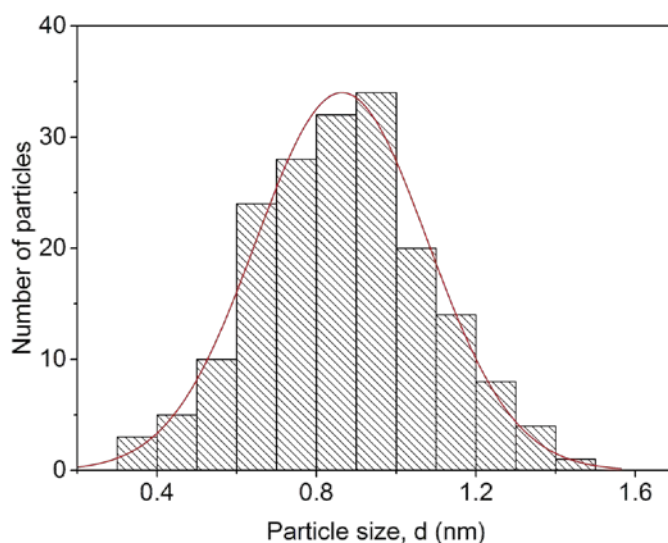


Figure 10 HAADF-STEM images of zeolite samples reduced with hydrazine for (a) 70 min, (b) 190 min, (c) 280 min, (d) and (d') 430 min and (e) 960 min. The bright spots represent copper nanoparticles

(A)



(B)

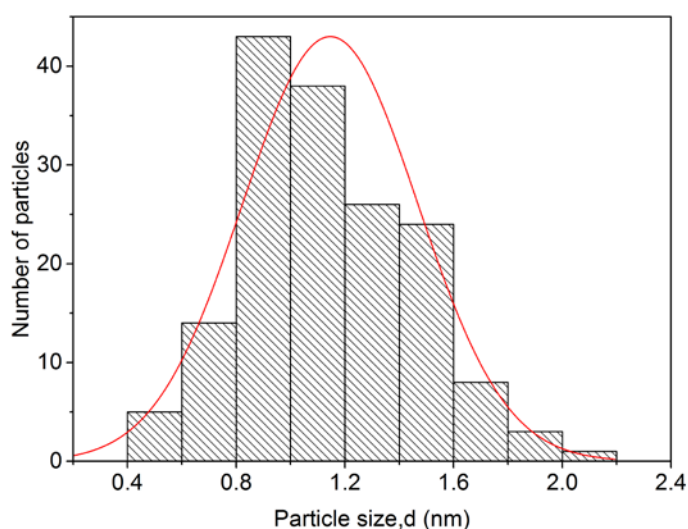


Figure 11 The histograms of copper particle size distribution of zeolite samples reduced with hydrazine for (A) 190 min, (B) 280 min with

As has been stated in the introduction, the thermal and air stability of the Cu NPs particles is of great importance for major applications, such as catalysis. To study the stability of Cu NPs in LTL nanocrystals, Cu⁰-LTL-280 min sample has been chosen as the most relevant. The air stability of the copper nanoparticles has been monitored using DR UV-vis. The spectra of self-supported pellets of copper-containing LTL have been recorded first (i) after storing the sample in Ar atmosphere and the second (ii) after storing in air for 48 hours (Figure 12).

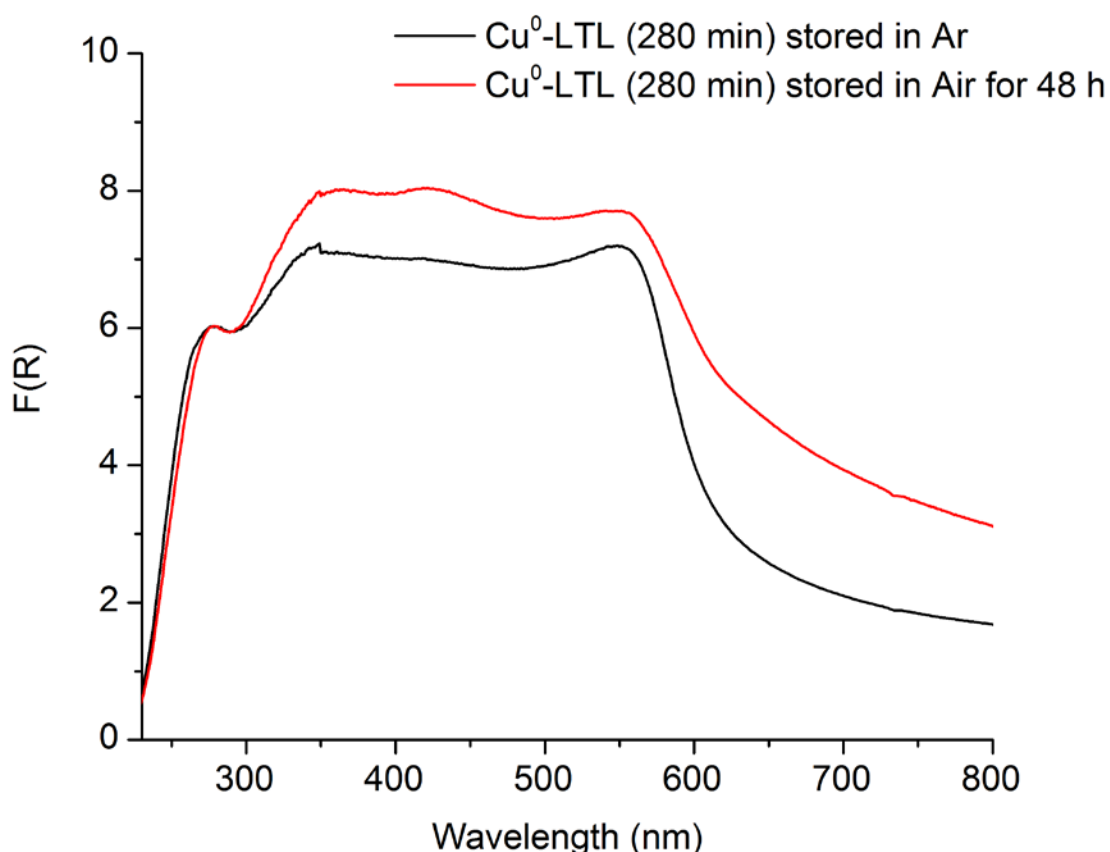


Figure 12 UV-vis spectra of self-supported pellets of copper-containing LTL recorded after storing the sample in Ar atmosphere (black) and after storing in air for 48 hours (red). A new peak at 420 nm assigned to Cu_2O ⁶¹ appeared in the red spectrum

As can be seen, a new peak at 420 nm, which can be assigned to Cu_2O ,⁶¹ appeared in the spectrum of the second sample.

Conclusions

A detailed study of the evolution of copper species in the LTL nanosized zeolite suspension during reduction with various reducing agents is presented. The use of sodium borohydride led to the rapid formation of large cubic shaped copper nanoparticles outside the zeolite crystals, while the reaction with triethylamine did not result in the formation of copper nanoparticles (Cu NPs). On the contrary, the copper cations were successfully reduced to Cu NPs with a uniform dispersion within the zeolite crystals when hydrazine was applied as the reducing agent. The dimension of the Cu NPs in the zeolite is limited by the size of zeolite channels and cages. With prolonged reduction time, the Cu NPs tend to migrate to the zeolite

surface due to their high mobility in aqueous media. On the other hand, for the particles located on the external surface of the zeolite crystals, the growth mechanism is more likely driven by the colloidal stability of the latter, thus resulting in large copper particles. Transmission electron microscopy shows the presence of 0.2-1.6 nm Cu NPs distributed throughout the zeolite crystals after 190 min. After 280 min there are more Cu NPs formed within the zeolite pores and on their surface with the maximum size of 2.2 nm. Finally, larger copper particles formed on the zeolite surface, while the zeolite structure is preserved. Further insight into the mechanism of the copper NPs formation allows to produce the materials with desired properties under controlled conditions. By tailoring the reduction time, it is possible to isolate supported copper nanoparticles with diverse sizes homogeneously distributed within the zeolite matrix. This enables to design the materials for applications such as catalysis and plasmon-mediated chemistry requiring well defined particle size.

References

- 1 Y. Lu and W. Chen, *Chem. Soc. Rev.*, 2012, **41**, 3594–623.
- 2 K. Jug, B. Zimmermann, P. Calaminici and A. M. Köster, *J. Chem. Phys.*, 2002, **116**, 4497–4507.
- 3 Y. Lu, W. Wei and W. Chen, *Chinese Sci. Bull.*, 2012, **57**, 41–47.
- 4 C. Vázquez-Vázquez, M. Bañobre-López, A. Mitra, M. A. López-Quintela and J. Rivas, *Langmuir*, 2009, **25**, 8208–16.
- 5 X. Crispin, C. Bureau, V. Geskin, R. Lazzaroni and J.-L. Brédas, *Eur. J. Inorg. Chem.*, 1999, **1999**, 349–360.
- 6 Y. Wang, P. Chen and M. Liu, *Nanotechnology*, 2006, **17**, 6000–6006.
- 7 Y. Sun, *Mater. Today*, 2012, **15**, 140–147.
- 8 Y. Sun, *Chem. Soc. Rev.*, 2013, 2497–2511.
- 9 S. Wang, X. Huang, Y. He, H. Huang, Y. Wu, L. Hou, X. Liu, T. Yang, J. Zou and B. Huang, *Carbon N. Y.*, 2012, **50**, 2119–2125.
- 10 T. V. W. Janssens, H. Falsig, L. F. Lundegaard, P. N. R. Vennestrøm, S. B. Rasmussen, P. G. Moses, F. Giordanino, E. Borfecchia, K. A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin and P. Beato, *ACS Catal.*, 2015, **5**, 2832–2845.
- 11 A. Corma, A. E. Palomares, F. Rey and F. Marquez, *J. Catal.*, 1997, **170**, 140–149.
- 12 G. Meitzner and E. Iglesia, *Catal. Today*, 1999, **53**, 433–441.
- 13 A. Gallo, T. Tsoncheva, M. Marelli, M. Mihaylov, M. Dimitrov, V. Dal Santo and K. Hadjiivanov, *Appl. Catal. B Environ.*, 2012, **126**, 161–171.
- 14 D. K. Kim and E. Iglesia, *J. Phys. Chem. C*, 2008, **112**, 17235–17243.
- 15 V. V. Ordonsky, M. Cai, V. Sushkevich, S. Moldovan, O. Ersen, C. Lancelot, V. Valtchev and a. Y. Khodakov, *Appl. Catal. A Gen.*, 2014, **486**, 266–275.
- 16 G. Yang, N. Tsubaki, J. Shamoto, Y. Yoneyama and Y. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 8129–8136.
- 17 V. Z. Fridman, A. A. Davydov and K. Titievsky, *J. Catal.*, 2004, **222**, 545–557.
- 18 R. S. Rao, A. B. Walters and M. A. Vannice, *J. Phys. Chem. B*, 2005, **109**, 2086–92.
- 19 J. Kecht, Z. Tahri, V. De Waele, M. Mostafavi, S. Mintova and T. Bein, *Chem. Mater.*, 2006, **18**, 3373–3380.
- 20 N. Cioffi, N. Ditaranto, L. Torsi and L. Sabbatini, *Approaches to synthesis and characterization of spherical and anisotropic copper nanomaterials*, 2009.
- 21 D. Farrusseng and A. Tuel, *New J. Chem.*, 2016.
- 22 J. Shi, Y. Wang, W. Yang, Y. Tang and Z. Xie, *Chem. Soc. Rev.*, 2015, **44**, 8877–8903.
- 23 A. Mazzocut, E. Coutino-Gonzalez, W. Baekelant, B. Sels, J. Hofkens and T. Vosch, *Phys. Chem. Chem. Phys.*, 2014, **16**, 18690–3.
- 24 S. Mintova, M. Jaber and V. Valtchev, *Chem. Soc. Rev.*, 2015, **44**, 7207–7233.
- 25 T. M. D. Dang, T. T. T. Le, E. Fribourg-Blanc and M. C. Dang, *Adv. Nat. Sci. Nanosci. Nanotechnol.*, 2011, **2**, 15009.
- 26 M. Severance and P. K. Dutta, *J. Phys. Chem. C*, 2014, **118**, 28580–28591.
- 27 M. Hölzl, S. Mintova and T. Bein, *Stud. Surf. Sci. Catal.*, 2005, **158**, 11–18.
- 28 G. S. Pawley, *J. Appl. Crystallogr.*, 1981, **14**, 357–361.
- 29 P. O. Fritz, J. H. Lunsford and C.-M. Fu, *Zeolites*, 1988, **8**, 205–208.
- 30 B. Abdolpour, M. Saeed and K. Sanaz, *Monatshefte für Chemie - Chem. Mon.*, 2016, 2–7.
- 31 P. H. Bolt, F. H. P. M. Habraken and J. W. Geus, *J. Solid State Chem.*, 1998, **69**, 59–69.
- 32 C. Hu, K. Shih and J. O. Leckie, *J. Hazard. Mater.*, 2010, **181**, 399–404.
- 33 L. M. Plyasova, T. M. Yur, I. Y. Molina, T. A. Kriger, A. M. Balagurov, L. P.

- Davydova, V. I. Zaikovskii, G. N. Kustova, V. V Malakhov and L. S. Dovlitova, *Kinet. Catal.*, 2010, **41**, 429–436.
- 34 S. M. Auerbach, K. A. Carrado and P. K. Dutta, *Handbook of zeolite science and technology*, CRC Press, 2004, vol. 2004.
- 35 P. Vanelderen, J. Vancauwenbergh, B. F. Sels and R. A. Schoonheydt, *Coord. Chem. Rev.*, 2013, **257**, 483–494.
- 36 R. Desai, V. Mankad, S. K. Gupta and P. K. Jha, *Int. J. Nanosci.*, 2012, 121102044327005.
- 37 U. Kreibig, M. Quinten and D. Schoenauer, *Optical Properties of Nanoparticle Systems*, 1986, vol. T13.
- 38 J. Polte, *CrystEngComm*, 2015, **17**, 6809–6830.
- 39 A. N. Pestryakov, V. P. Petranovskii, A. Kryazhov, O. Ozhereliev, N. Pfänder and A. Knop-Gericke, *Chem. Phys. Lett.*, 2004, **385**, 173–176.
- 40 V. De Waele, J. Kecht, Z. Tahri, M. Mostafavi, T. Bein and S. Mintova, *Sensors Actuators B Chem.*, 2007, **126**, 338–343.
- 41 B. G. Ershov, E. Janata, M. Michaelis and a Henglein, *J. Phys. Chem.*, 1991, **95**, 8996–8999.
- 42 J. Khatouri, M. Mostafavi, J. Amblard and J. Belloni, *Chem. Phys. Lett.*, 1992, **191**, 351–356.
- 43 M. Salavati-Niasari and F. Davar, *Mater. Lett.*, 2009, **63**, 441–443.
- 44 Y. Yu, L. Zhang, J. Wang, Z. Yang, M. Long, N. Hu and Y. Zhang, *Nanoscale Res. Lett.*, 2012, **7**, 347.
- 45 J. D. S. Newman and G. J. Blanchard, *Langmuir*, 2006, **22**, 5882–7.
- 46 P.-L. Kuo and C.-C. Chen, *Langmuir*, 2006, **22**, 7902–6.
- 47 M. Zaarour, B. Dong, I. Naydenova, R. Retoux and S. Mintova, *Microporous Mesoporous Mater.*, 2014, **189**, 11–21.
- 48 M. Grouchko, A. Kamysny, K. Ben-Ami and S. Magdassi, *J. Nanoparticle Res.*, 2007, **11**, 713–716.
- 49 R. Sierra-Ávila, M. Pérez-Alvarez, G. Cadenas-Pliego, V. C. Padilla, C. Ávila-Orta, O. P. Camacho, E. Jiménez-Regalado, E. Hernández-Hernández and R. M. Jiménez-Barrera, *J. Nanomater.*, 2015, **2015**, 1–9.
- 50 N. G. Bastus, J. Piella and V. Puntès, *Langmuir*, 2016, **32**, 290–300.
- 51 A. R. Tao, S. Habas and P. Yang, *Small*, 2008, **4**, 310–325.
- 52 A. Tao, P. Sinsermsuksakul and P. Yang, *Angew. Chemie - Int. Ed.*, 2006, **45**, 4597–4601.
- 53 Q. Liu, M. R. Gao, Y. Liu, J. S. Okasinski, Y. Ren and Y. Sun, *Nano Lett.*, 2016, **16**, 715–720.
- 54 N. T. K. Thanh, N. Maclean and S. Mahiddine, *Chem. Rev.*, 2014, **114**, 7610–7630.
- 55 P. K. Khanna, S. Gaikwad, P. V. Adhyapak, N. Singh and R. Marimuthu, *Mater. Lett.*, 2007, **61**, 4711–4714.
- 56 H. Awala, J.-P. Gilson, R. Retoux, P. Boullay, J.-M. Goupil, V. Valtchev and S. Mintova, *Nat. Mater.*, 2015.
- 57 <http://europe.iza-structure.org/IZA-SC/framework.php?STC=LTL>
- 58 F. Schröder, D. Esken, M. Cokoja, M. W. E. Van Den Berg, O. I. Lebedev, G. Van Tendeloo, B. Walaszek, G. Buntkowsky, H. H. Limbach, B. Chaudret and R. a. Fischer, *J. Am. Chem. Soc.*, 2008, **130**, 6119–6130.
- 59 F. W. H. Kampers, C. W. R. Engelen, J. H. C. Van Hooff and D. C. Koningsberger, *J. Phys. Chem.*, 1990, **94**, 8574–8578.
- 60 S. Turner, O. I. Lebedev, F. Schröder, D. Esken, R. a. Fischer and G. Van Tendeloo, *Chem. Mater.*, 2008, **20**, 5622–5627.

- 61 M. D. Susman, Y. Feldman, A. Vaskevich and I. Rubinstein, *Chem. Mater.*, 2012, **24**, 2501–2508.

Chapter 2

Formation of copper nanoparticles in LTL nanosized zeolite: spectroscopic characterization

Introduction

Metallic nanoparticles have attracted significant attention in catalysis science due to their high catalytic activity and selectivity in many important chemical processes such as hydrogenation/dehydrogenation¹, isomerization², oxidation and reduction of NO_x with hydrocarbons³. High catalytic activity is ascribed to a high proportion of atoms located at corners and edges that have low coordination numbers and the ability to activate substrates⁴. The number of such atoms is increasing with the decrease of particle size, and it has been frequently reported that the catalytic activity increased when the particle size decreased. Most active catalysts were those for which particles are below 5 nm⁴. Substantial progress has been achieved in the synthesis of silver and gold nanoparticles^{5,6}. In this context, copper nanoparticles (Cu NPs) with controlled size and shape are good alternative materials for catalysis, because of their high conductivity, catalytic properties, and lower price⁷. However, reports on copper nanoparticles are rather limited, primarily because of relatively low Cu⁰/Cu²⁺ redox potential (+0.34 V), which causes spontaneous oxidation at ambient conditions^{8,9}.

The main drawback of small metallic nanoparticles is low thermal stability and a tendency to sinter under harsh reaction conditions, limiting their application at a large scale. These obstacles can be overcome by confining the nanoparticles into the pores and/or cavities of inorganic supports.

Zeolites are promising hosts (matrix) for stabilization of metal nanoparticles⁴. The size, distribution and location of the nanoparticles are controlled by the steric constraints that originate from the zeolite topology, *i.e.* regular system of pores and cavities¹⁰. Additionally, the zeolite structure imposes shape selectivity by limiting the diffusion of the molecules with the effective diameter bigger than the pore openings. However, exactly the existence of strong confinements, giving on one hand the useful properties of the material, can simultaneously affect their performance in catalysis and separation processes due to the extremely slow mass transport through the micropores. Advances in synthesis of nanosized zeolites gives the materials in which the mean diffusion path is significantly lower, compared to their conventional micron-sized counterparts. Indeed, the combination of superior properties on nanosized zeolites with the exceptional reactivity of metallic nanoparticles opens a way to the design of new advanced catalytic materials¹¹.

In the previous chapter, we had investigated the formation of copper nanoparticles inside the nanosized LTL zeolite. The copper cations were introduced in zeolite nanocrystals via ion exchange after the synthesis directly in the suspensions.¹² Subsequently, the copper ions were treated with hydrazine monohydrate as a reducing agent. We had shown that by tailoring the synthesis conditions, it is possible to isolate supported copper nanoparticles with diverse sizes homogeneously distributed within the zeolite matrix. However, due to the nature of the synthesis process, where the reduction reaction is interrupted in order to obtain the copper nanoparticles of desired size, existence of various copper species should not be neglected. The necessity of having well defined and characterized, not just Cu nanoparticles (NPs), but also other copper species arises from the desired application, since the catalytic activity and selectivity can be affected by the presence of unwanted active sites. Hence, an accurate design of copper active sites and their complementary characterization are crucial steps in the rational preparation of Cu NPs supported zeolites catalysts.

FTIR spectroscopy of adsorbed probe molecules has been extensively used to determine the oxidation states of supported metal species.^{13–15} It is important to note that the choice of a suitable probe molecule is a crucial point in the FTIR spectroscopy as it determines which surface property will be probed.¹⁶ CO and NO probe molecules can provide highly valuable information on the supported metal dispersion and coordination, as well as on the oxidation degree of such species. Another positive point for the use of such probes is their small size, allowing site accessibility even in the small cavities/channels of zeolites.

In this work, the adsorption of CO and NO molecules on copper containing LTL type zeolite was investigated. The choice of CO was determined by its sensitivity towards Cu^+ sites, whereas the choice of NO was governed by the sensitivity to Cu^{2+} species. Experiments were performed at liquid-nitrogen temperature that allows to detect the sites characterized by a weak interaction with the probe and cannot be detected at higher temperatures.¹⁶

However, elucidating the nature of Cu species in zeolites is not an easy task and usually demands a multi-technical approach. For these reasons the FTIR studies have been complemented with EPR, ^{29}Si and ^{63}Cu MAS NMR and DR UV-Vis measurements. Indeed, EPR and ^{29}Si MAS NMR help to complement the information on the Cu^{2+} species and the changes in their environment, whereas the ^{63}Cu MAS NMR allows characterization of metallic copper species. Additionally, DR UV-Vis is used to characterize copper in both oxidation states, metallic copper and different Cu-O complexes.

Experimental

Nanosized LTL type zeolite with monomodal particle size distribution was synthesized as described elsewhere.¹² The as-prepared precursor suspensions were aged at room temperature for 24 hours prior to hydrothermal treatment at 170 °C for 18 hours. After the crystallization process was accomplished, the nanosized zeolite crystals were recovered by multistep centrifugation (20000 rpm, 40 min) and washed with doubly distilled water until pH = 7 – 8

(denoted parent LTL). Samples were ion-exchanged with copper nitrate (0.1 M) in colloidal zeolite suspensions, giving solutions containing 0.3 mmol Cu^{2+} /g zeolite to achieve ~10 % of K^+ cations exchange for copper. The ion-exchange process was carried out at room temperature for 2 hours, and then the solutions were purified by multi-step centrifugation to remove the excess of copper ions (this sample is denoted by Cu^{2+} -LTL), and finally incorporated copper cations were reduced in zeolite suspension using excess of hydrazine ($\text{Cu}^{2+}/1000 \text{ N}_2\text{H}_4$) under N_2 atmosphere. The reduction was carried out at room temperature for 280 minutes, which corresponds to ~56% reduction of Cu^{2+} to Cu^0 in obedience to UV-Vis *in situ* studies.¹² Subsequently the solids were freeze-dried. The final product was identified as Cu^0 -LTL and stored in the glove box in Ar atmosphere to prevent the Cu NPs from oxidation. According to HRTEM results, the copper nanoparticles are evenly distributed in the pores and on the surface of the LTL matrix with the mean size of 0.4-2.2 nm. The detailed description of the preparation procedure, the structural and textural characterization of the copper nanoparticles-LTL zeolite material is described and reported in our previous paper.¹²

FTIR spectra of CO and NO adsorption on self-supported zeolite pellets were recorded using a Thermo-Nicolet Nexus instrument by accumulation of 128 scans and a spectral resolution of 4 cm^{-1} . Self-supporting pellets ($d = 16 \text{ mm}$, $m = 20 \text{ mg}$) were prepared from the powder samples and studied using *in situ* transmission IR at ambient and low temperatures. Prior to the IR measurements, the samples were activated under oxygen or hydrogen atmosphere or in vacuum at 673 – 723 K, to study the effect of different oxidation and reducing pre-treatments steps on the state of copper species. After the pre-treatment, small calibrated doses of CO and NO were introduced into the IR cell up to an equilibrium pressure of 60 and 40 torr, respectively. Additionally, in the case of CO adsorption the system was subsequently evacuated at 100 K and at 423 K to investigate the stability of formed species.

The effective reduction of the copper species was studied by variable temperature pulsed EPR carried out at X-band (9.64 GHz) using a Bruker ELEXSYS E580 FT spectrometer. The state of copper was also characterized by diffuse reflectance UV-Vis spectroscopy utilizing a Varian Cary 4000 spectrophotometer. Additionally, ^{63}Cu and ^{29}Si MAS NMR spectra were recorded by Bruker 500 MHz spectrometer.

Results and discussion

FTIR spectroscopy

The FTIR spectra (OH stretching region) of the Cu^{2+} -LTL and Cu^0 -LTL samples after activation in vacuum at 673 K are presented in Figure 1. Both materials contain the bands at $3747\text{--}3744\text{ cm}^{-1}$, which are characteristic of the isolated external silanol groups.¹⁶ High relative intensity of these bands reflects the low size of the crystals that has already been reported in the literature as the spectral characteristic of the nanosized zeolites. The Cu^0 -LTL sample exhibits additional bands at 3661 and 3628 cm^{-1} , that can be assigned to extra framework Al-sites and bridged hydroxyl $\equiv\text{Si}(\text{OH})\text{Al}\equiv$ groups, respectively.^{15–17} These bands are the consequence of the chemical reduction and high temperature activation of this sample. The presence of the latter can be explained by occupation of the vacant structure charge balancing positions with proton after the reduction of Cu^{2+} species to Cu^0 . Appearance of extra framework aluminum can then be explained by the partial distortion of the LTL structure. This phenomena is often observed for zeolites with low Si/Al ratios as already reported in the literature¹⁸. However, it should be noticed that this effect is not dominant, as the intensity of the latter bands is not high.

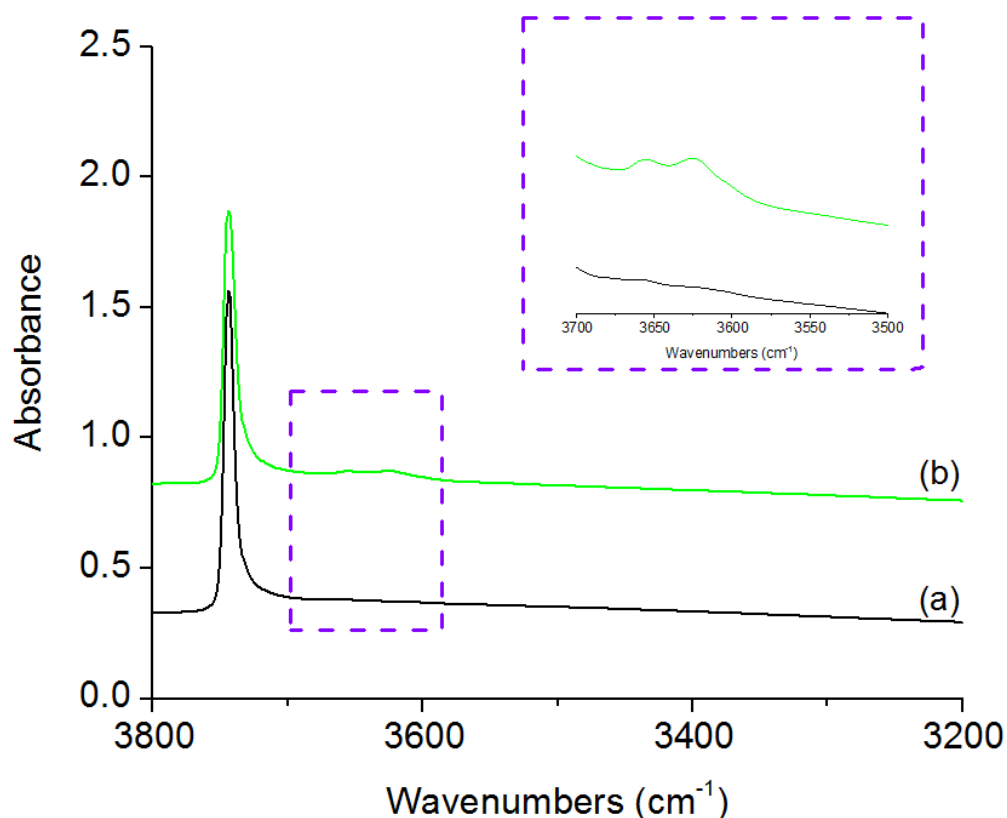


Figure 1 FTIR spectra of samples after activation in OH-region at RT: (a) Cu^{2+} -LTL and (b) – Cu^0 -LTL. Insert: IR spectra in the region $3500\text{--}3700\text{ cm}^{-1}$

CO adsorption on copper-LTL samples followed by FTIR spectroscopy

The state of the copper species in the ion-exchanged zeolites is of primary importance for their possible catalytic applications. It is thus necessary to control as finely as possible not only the amount of the desired sites (copper nanoparticles), which are necessary to realize the targeted reaction but also to hinder as much as possible the number and action of the undesired ones, such as various Cu^{1+} and Cu^{2+} species.

CO is a small molecule that forms a donor bond to the metal centres. FTIR spectroscopy is used to study the carbonyl complex formed with transition metal cations by their carbonyl stretching frequency that responds very sensitively to coordination onto cationic sites, shifting the frequency of gaseous CO at 2143 cm^{-1} . The frequency shifts give information about the oxidation and coordination state of the cation. In the case of copper, CO is

preferentially adsorbed over Cu^{1+} ions since the formed carbonyl complex is stabilized by π -back donation while no stable carbonyls are formed with the participation of Cu^{2+} ions at room temperature.¹⁹ Additionally, CO forms mainly a π -bond with Cu^0 atoms, and the resulting complexes are unstable. Frequencies of Cu^{1+} -CO and Cu^0 -CO fall in the same spectral region, 2110-2080 cm^{-1} , which makes their discrimination hard. However, the goal of this work is not to detect the nanoparticles, since they have been already identified and characterized in our previous article,¹² but to characterize the residual copper species that may have influence on their potential applications.

The adsorption of CO on copper containing zeolite samples was initially studied at low temperature (100 K) by introduction of calibrated doses of CO from 5 to 60 torr. Figure 2A-D shows the IR spectra (C-O-stretching region) of the Cu^{2+} -LTL sample pre-treated in oxygen (a), vacuum (b) or hydrogen (c), and Cu^0 -LTL sample pre-treated in vacuum at the same temperature (d). For convenience, the observed CO stretching frequencies are summarized in Table 1. Different pre-treatment conditions were used to monitor the behaviour of copper that will help to determine the spectral features ascribed to specific species.

Careful spectral deconvolution of all spectra has permitted the differentiation of the number of overlapped components with close maxima but different half width and allowed to see their evolution with increasing of the CO pressure. The deconvolution has been performed with MagicPlot software using Gaussian function. The peak positions have been determined using the second derivative and were fixed for all spectra in order to fit properly the $\nu(\text{CO})$ band.

Adsorption of CO (5 – 20 torr) on the Cu^{2+} -LTL sample, activated under O_2 atmosphere, (Figure 2A) leads to the appearance of intense bands at 2140 and 2128 cm^{-1} attributed to Cu^+ -CO complexes at different locations in the zeolite framework, characterized by different stability towards evacuation that will be shown further.²⁰ The low intensity band at 2190 cm^{-1}

can be assigned to $\text{Cu}^{2+}\text{-CO}$ species.²¹ After introduction of the 20 torr of CO, two bands at 2163 and 2150 cm^{-1} with a peak shoulder at 2121 cm^{-1} , that rise simultaneously at higher coverages, are also detected. These bands are contributed to C-O-stretching of $\text{K}^+\cdots\text{CO}$ adducts and oxygen-bonded CO according to previous reports.^{13,22} The band at 2163 cm^{-1} could be also ascribed as the interaction of CO with the silanol OH groups at low temperature.¹³ The uprising of the peak shoulder at 2177 cm^{-1} manifest the interaction of CO with bridging OH groups or, which is more likely in this system, the formation of the dicarbonils $\text{Cu}^+(\text{CO})_2$ complexes,¹³ since no OH bridging groups are observed for the oxidized samples (Fig. 1).

Table 1 Assignment of the C–O stretching frequencies observed in the copper containing zeolite samples

No.	Species	Mode	Frequency, cm^{-1}	Notes
1	$\text{Cu}^+\text{-CO}$	$\nu(\text{CO})$	2140	Populated first, stable upon evacuation at RT
			2128	Populated first, stable upon evacuation at 423 K
2	$\text{Cu}^+(\text{CO})_2$	$\nu_s(\text{CO})$	2177	Appear at high coverage at 100 K,
		$\nu_{as}(\text{CO})$	2150	not stable upon evacuation
3	$\text{Cu}^0\text{-CO}$	$\nu(\text{CO})$	2103	Unstable upon evacuation at 100 K
4	$\text{Cu}^{2+}\text{-CO}$	$\nu(\text{CO})$	2190	Unstable upon evacuation at 100 K
5	$\text{K}^+\text{-CO}$	$\nu_s(\text{CO})$	2163	Appears at higher coverage at 100
			2150	K, unstable upon evacuation
			2121	Oxygen-bonded CO
6	$\text{Al}^{3+}\text{-CO}$	$\nu(\text{CO})$	2230	Appear at 100 K, unstable upon evacuation
7	OH-group	$\nu(\text{CO})$	2163	Interaction with silanol group
			2177	Interaction with bridging OH group

The IR spectra collected for the Cu^{2+} -LTL sample, activated at 673 K in vacuum are similar (Figure 2B). However, the evolution of their intensities with the coverage level differs significantly. The bands at 2140, 2128 and 2177 cm^{-1} , assigned to $\text{Cu}^{1+}\text{-CO}$ and $\text{Cu}^{1+}(\text{CO})_2$, appear first, whereas the peaks at 2190, 2163 and 2150 cm^{-1} appear at higher coverage after introduction of 20 torr CO. There is a peak at 2103 cm^{-1} , which becomes evident only after

deconvolution, that appears at high coverage and generally is assigned to the formation of Cu^0 species.¹³ By comparing the spectra in Figures 2 A and B, significant oxidation of Cu^{1+} to Cu^{2+} in O_2 atmosphere can be observed, however Cu^{1+} species are still preserved. The high amount of Cu^{1+} -CO and the presence of Cu^0 -CO species in the sample treated in vacuum can be explained by so called “self-reduction” of Cu^{2+} at high temperature because of the dehydration of the divalent $\text{Cu}^{2+}(\text{H}_2\text{O})_n$ complexes, as their formation is favored upon the ion exchange procedure.^{23,24} The IR spectra for Cu^{2+} -LTL sample pre-treated in H_2 and Cu^0 -LTL sample, reduced with hydrazine and pre-treated at 723 K in vacuum are shown in Figure 2C and Figure 2D, respectively. These two samples display almost identical spectra with similar band intensities. The main difference from the previous spectra (Figure 2A, B) is the lower intensity of the bands at 2190 and 2177 cm^{-1} that belong to Cu^{2+} -CO, Cu^+ dicarbonils and possibly to bridging OH groups. This is obviously the consequence of the reduction treatment applied to these two samples, and the very weak interaction of CO with the Cu^{2+} oxidation state. Another important difference (see Figure 2B), is the lower intensity of the bands at 2140 and 2128 cm^{-1} (Cu^{1+} -CO) and more pronounced peak at 2103 cm^{-1} , assigned to the Cu^0 -CO, that appears at lower pressure. Taking this into account and having in mind that the amount of copper is the same in all samples these spectral changes can be assigned to the CO coordination with CuNPs. This result agrees with the literature data, that shows that high temperature treatment with hydrogen of copper exchanged zeolites leads to the formation of Cu nanoparticles (CuNP). In addition, this is in agreement with our findings,¹² that interaction of Cu^{2+} -LTL sample with hydrazine in aqueous phase creates CuNP. The stability of copper carbonyls was further investigated. The decrease of the CO equilibrium pressure by progressive evacuation at 100 K (Figure 3A-D), and at higher temperatures leads to the diminution of most of the bands.

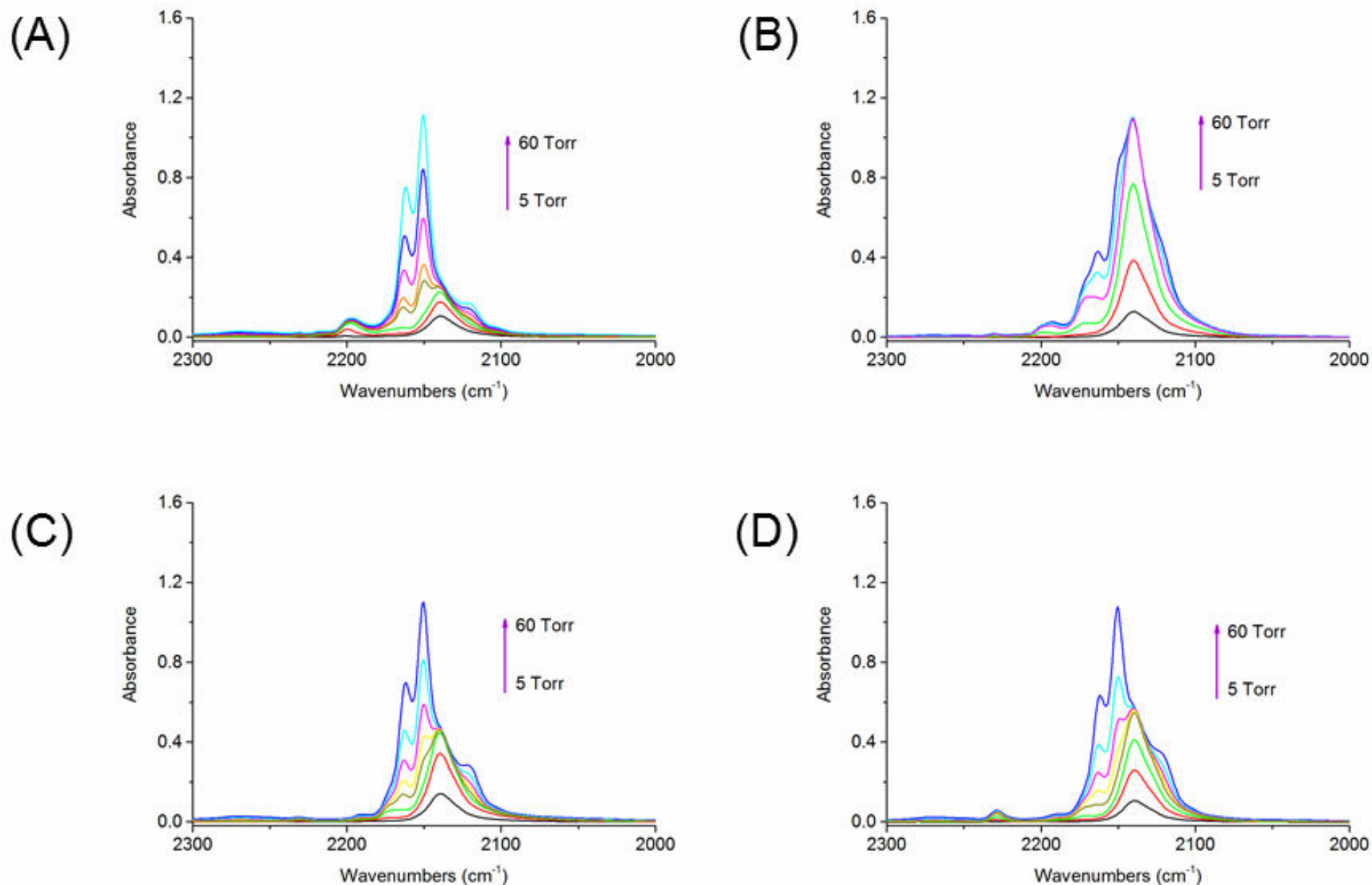


Figure 2 Evolution of the IR spectra in the 2300-2000 cm^{-1} range with increasing doses of CO at 100 K. Sample activated in O_2 (A), vacuum (B), H_2 (C), and Cu^0 -LTL sample in vacuum (D) at 673 K

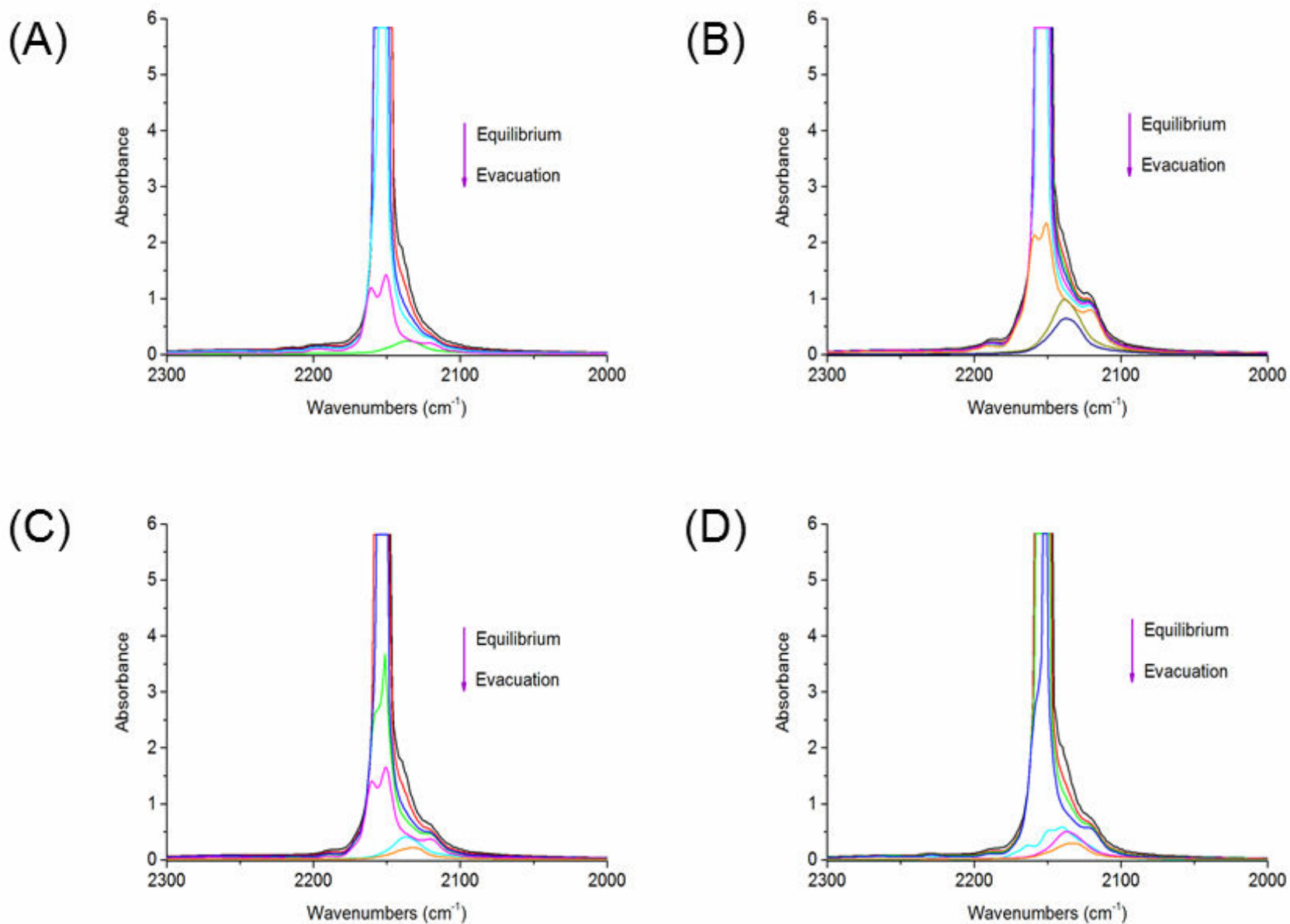


Figure 3 Evolution of the IR spectra in the range 2300–2000 cm^{-1} upon evacuation at 100 K and activation at 673 K for Cu^{2+} -LTL sample in O_2 (A), vacuum (B), H_2 (C), and Cu^0 -LTL in vacuum (D)

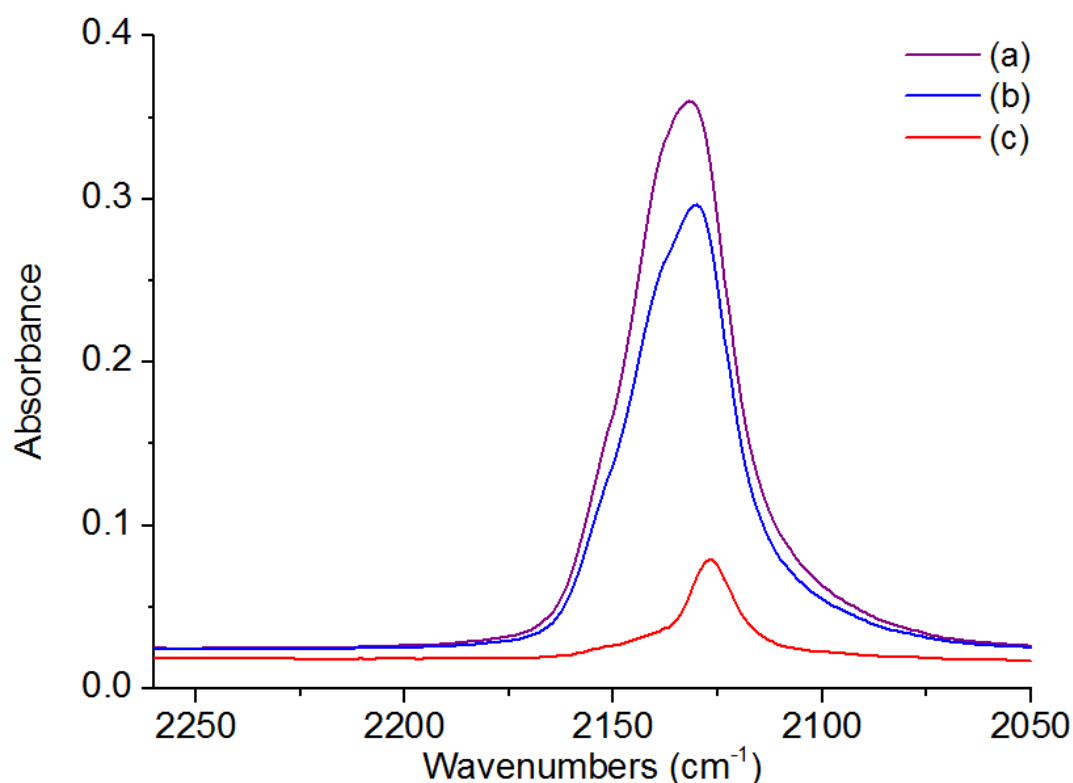


Figure 4 Evolution of the IR spectra (2300-2000 cm^{-1}) of the Cu^0 -LTL sample prepared with hydrazine and activated at 723 K in vacuum upon evacuation at RT (a), after 10 min at RT (b) and after heating at 423 K (c)

Only the bands at 2140 and 2128 cm^{-1} , attributed to Cu^+ -CO complexes (Figure 4), remain after evacuation at ambient temperature. However, after evacuation at 423 K pronounced peak at 2128 cm^{-1} still remains while the intensity of the band at 2140 cm^{-1} decreases drastically.¹³ It should also be noted that all samples before and after reduction contain Cu^+ -species that are the first to be populated with introducing CO.

If the made assumptions are correct that the transition moment for $\nu(\text{CO})$ adsorbed on a particular site is independent of the pre-treatment conditions, then the change in relative intensities of the IR bands can be associated with changes in the relative numbers of sites.²⁰ Though, FTIR spectroscopy of adsorbed CO allows the estimation of the dispersion of Cu^{1+} sites in the samples and determination of the $\text{Cu}^+/\text{Cu}_{\text{total}}$ ratio, based on the number of

adsorbed CO molecules at the Cu⁺ species saturation. The integrated areas of the $\nu(\text{CO})$ band at 2140 and 2128 cm⁻¹ were calculated after deconvolution of the recorded pattern (Figure 5A). Assuming the CO molar adsorption coefficient for the band at 2140 cm⁻¹ is 13.5 cm/ μmol and for the band at 2128 is 10 cm/ μmol ,¹³ and the surface of the pellet is 2 cm², the concentration of Cu¹⁺ species was calculated by the following equation:

$$n = \frac{\text{Area} \times S_{\text{pellet}}}{\varepsilon \times m_{\text{pellet}}},$$

where n is the concentration of Cu¹⁺ (mol/g);

Area is from the CO adsorption bands at 2140 and 2128 cm⁻¹ obtained after the deconvolution (cm⁻¹);

ε is molar absorption coefficient of CO on Cu¹⁺ (cm/mol);

S_{pellet} is the surface of the pellet (2 cm²);

m_{pellet} is the mass of the pellet (g).

The evolution of the integrated area of the $\nu(\text{CO})$ band at 2140 cm⁻¹ as a function of the introduced CO displays an increment followed by a plateau as shown in Figure 5B. Therefore, considering the Cu⁺ : CO stoichiometry to be 1 : 1,²⁵ the CO adsorption monolayer on Cu⁺ can be determined by intersection of two trend lines built on the slope and plateau. The results for the series of samples after different pre-treatment are reported in Table 2. The high stability of Cu⁺ in the zeolites is clearly observed, while Cu⁺ is presented in all the samples in significant amounts. The quantity of Cu⁺ species in the Cu⁰-LTL sample is 44% from the total copper present in the sample, which is in agreement with the UV-Vis measurements¹² that showed that the relative amount of Cu⁰ species was 56% with respect to the total copper loading.

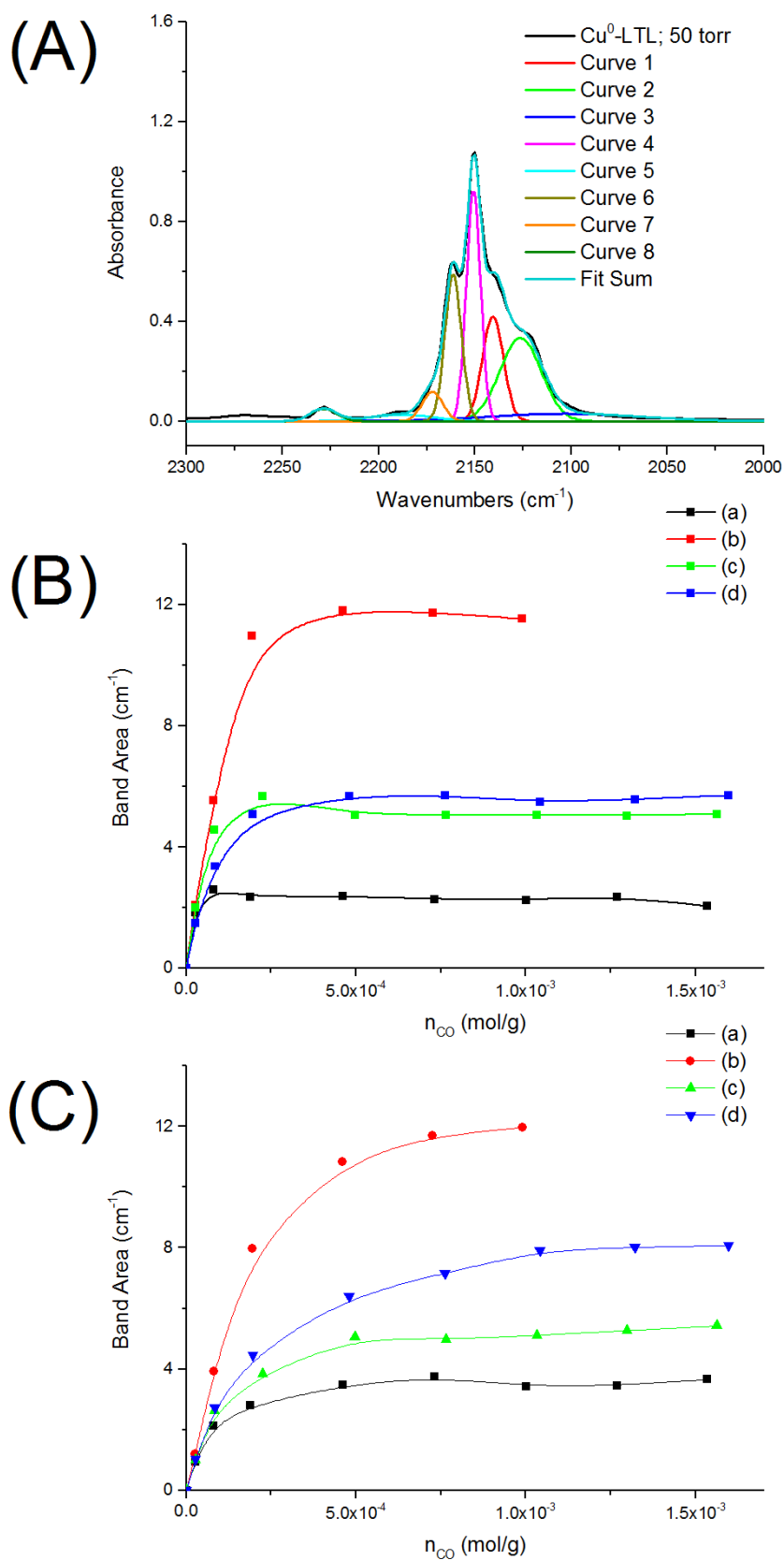


Figure 5 (A) Peak deconvolution for sample Cu⁰-LTL activated at 723 K in vacuum under CO (50 torr). (B) Integrated area of the ν(CO) band at 2140 cm⁻¹ and (C) integrated area of the ν(CO) band at 2128 cm⁻¹ bound to copper as a function of the CO introduced for a set of samples: Cu²⁺-LTL activated at 673 K in O₂ (a), (b) Cu²⁺-LTL activated at 673 K in vacuum, (c) Cu²⁺-LTL activated at 673 K in H₂ and (d) Cu⁰-LTL activated at 723 K in vacuum.

Table 2 Evaluation of number of Cu⁺ sites with respect to the total amount of copper in the samples based on IR study

Sample	m _{pellet} , g	Area at 2140 cm ⁻¹	Area at 2128 cm ⁻¹	n _{CO} , mol/g	n _{Cu⁺} , mol/g	m _{Cu⁺} , g	m _{Cu} , g	Cu ¹⁺ (2140 cm ⁻¹), %	Cu ¹⁺ (2128 cm ⁻¹), %
(a)	0.01958	2.59	2.13	8.05E-05	2.93E-05	3.65E-05	2.43E-04	10.09	11.19
(b)	0.01958	10.98	7.97	1.94E-04	12.42E-05	15.45E-05	2.43E-04	42.78	41.92
(c)	0.01958	5.69	3.84	2.25E-04	6.43E-05	8.00E-05	2.43E-04	22.16	20.24
(d)	0.01941	5.08	4.47	1.97E-04	5.79E-05	7.14E-05	2.41E-04	19.95	23.73

NO adsorption on copper-LTL samples followed by FTIR spectroscopy

The Cu^{2+} cations form stronger bonds with NO than with CO. As a result, surface Cu^{2+} -NO species are easily formed at room temperature and detected in the spectral region 1964-1845 cm^{-1} . NO bonds predominantly are formed by a σ -bond to the cations, and the higher the N-O stretching frequency the stronger is the bond. On the other side, NO molecule has one more electron than CO, which makes π -back donation more difficult. As a result, the Cu^+ -NO species are not stabilized by a σ - π synergistic effect and are considered unstable.¹⁹ It should also be mentioned that to the best of our knowledge there is no literature data published on the interaction of nitric oxide with copper nanoparticles using FTIR.

The adsorption of calibrated doses of NO from 10 to 40 torr at low temperature on the same series of samples, pre-treated in the same way as for the CO adsorption, was performed. The IR spectra contain the groups of bands in the region 1980–1850 cm^{-1} (Figure 6A-D) and the region 1850 – 1650 cm^{-1} (Figure 6 (a, b)).¹⁴ The bands and the corresponding assignments are summarized in Table 2.

The bands at 1953, 1938, 1905, 1886 cm^{-1} are characteristic for Cu^{2+} -NO species and correspond to probably four different Cu^{2+} sites. According to the literature,^{14,26} the intense bands at lower frequencies can be assigned to isolated Cu^{2+} ions, while the bands at higher frequencies belong to nitrosyls formed with associated Cu^{2+} -O- Cu^{2+} sites or isolated Cu^{2+} cations in the square planar coordination. As shown in Figure 6A, B, the intensity of the bands with lower frequency (1886 cm^{-1}) are less affected by treatment of the sample in vacuum or in H_2 than the ones at higher frequency. Indeed, the isolated Cu^{2+} sites are expected to be more difficult to reduce.^{27–29} The second set of bands includes peaks at 1825, 1810, 1797 and 1730 cm^{-1} , that generally represent the interaction of NO with Cu^+ -sites.¹⁴ They can be assigned as follows: the peaks at 1810 and 1797 cm^{-1} correspond to Cu^+ -NO mono-nitrosyls, that has been previously observed in zeolite Y, that evolve with increasing

pressure to $\text{Cu}^+(\text{NO})_2$ di-nitrosyls characterized by doublet with ν_s and ν_{as} at 1825 and 1730 cm^{-1} .^{14,29} In general, the behaviour of NO adsorption on Cu^+ species in the samples follows the same trend as for CO adsorption. There is a significant increase in the amount Cu^+ species for the sample prepared in vacuum compared to the one pre-treated in O_2 . For the sample reduced under H_2 and Cu^0 -LTL sample pre-treated in vacuum, there is an evident decrease in the bands associated with Cu^+ and Cu^{2+} species. This can be again attributed to the formation of metallic nanoparticles (CuNP) that do not interact with NO molecules. However, spectral lines associated to both (1+) and (2+) copper oxidation states are still present.

It should also be mentioned that other bands were observed. The bands at 1770 and 1863 cm^{-1} stay for *cis*-(N_2O_2) weakly adsorbed in the zeolite channels, that appear due to isomerisation of NO at low temperatures.^{17,27,30} The peaks centred at 1886 and 1874 cm^{-1} become visible for the Cu^0 -LTL sample, which are assigned to $\text{K}^+\cdots\text{NO}$ monomers (Figure 6C).¹⁷ The latter are masked in the case of the Cu^{2+} -LTL pre-treated in O_2 or under vacuum by Cu^{2+} -NO species (Figure 6A, B). All four samples contain the peak at 2245 cm^{-1} , that has been previously described as weakly bonded N_2O with the zeolite.¹⁷ The peaks centred at 1683, 1712 and 1749 cm^{-1} , in its turn, can be attributed to N_2O_4 or NO_2 . The band at 1749 cm^{-1} is typical of N_2O_4 adsorbed on zeolite acidic hydroxyls, as can be seen this band is more pronounced in case of the reduced and self-reduced samples. The later confirms the assumption concerning the occupation of the vacant structure charge balancing positions with proton after the reduction of Cu^{2+} species to Cu^0 . The presence of various N_xO_y in the spectra should be explained by NO disproportion or by the contamination of the NO. It is known that the following equilibrium exists for NO: $3\text{NO} \rightleftharpoons \text{NO}_2 + \text{N}_2\text{O}$, that is shifted to the right at higher pressures. Also, NO_2 is known to be easily dimerized to N_2O_4 .¹⁴

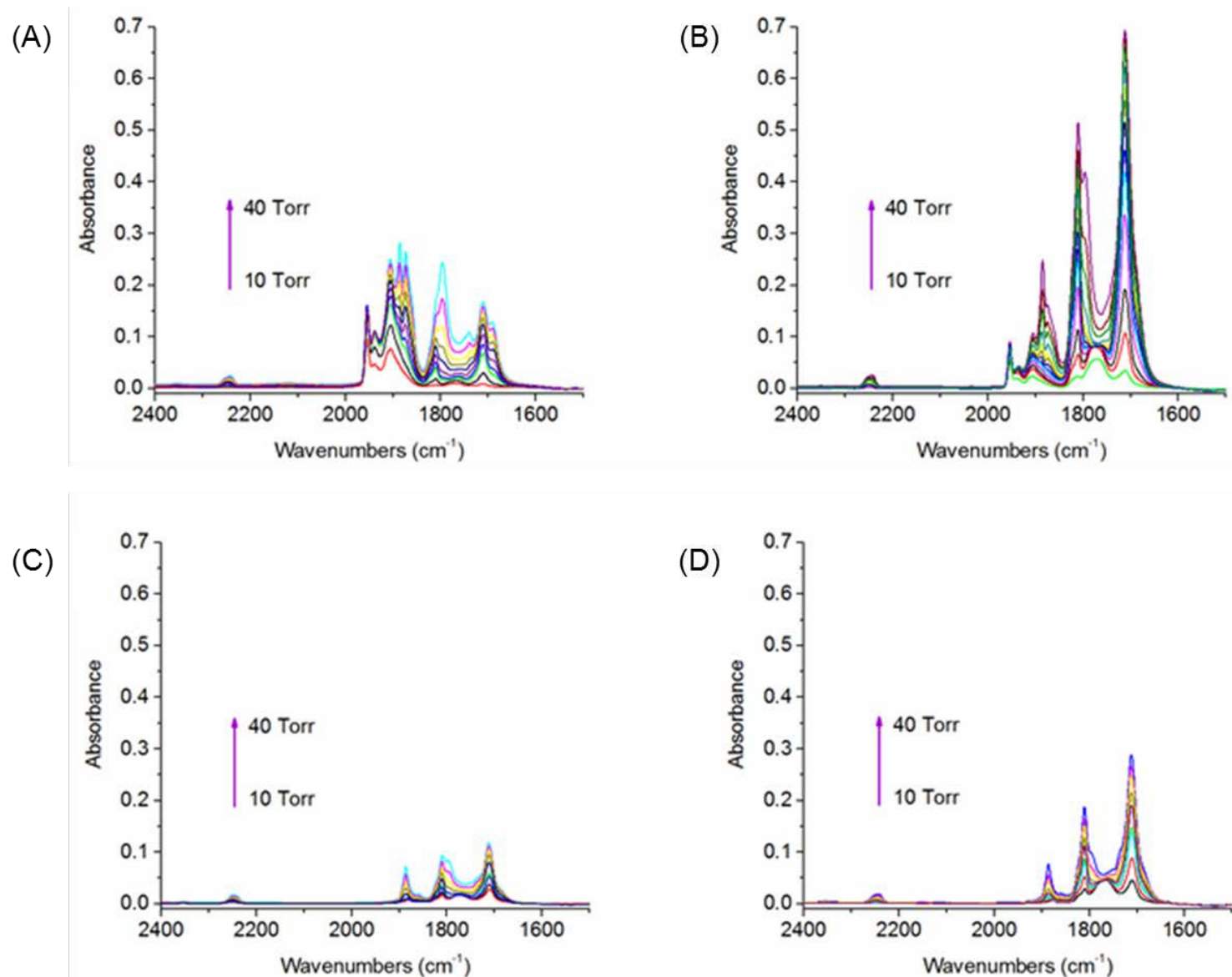


Figure 6 Evolution of the IR spectra in the 2400-1500 cm⁻¹ range upon interaction with increasing doses of NO at 100 K. Sample Cu²⁺-LTL activated at 673 K in O₂ (A), sample activated at 673 K in vacuum (B), sample activated at 673 K in H₂ (C), and reduced sample Cu⁰-LTL with N₂H₄ activated at 723 K in vacuum (D).

Table 3 Assignment of the N–O stretching frequencies observed in this study

No.	Species	Mode	Frequency, cm ⁻¹	Notes
1	Cu ⁺ -NO	v(NO)	1797 1810	Converts to dinitrosyls, not stable upon evacuation
2	Cu ⁺ -(NO) ₂	v _s (NO) v _{as} (NO)	1825 1730	Appear at high coverage at 100 K, not stable upon evacuation
3	Cu ²⁺ -NO	v(NO)	1955 1938 1905 1886	Correspond to associated Cu ²⁺ sites, unstable upon evacuation at 100 K Cu ²⁺ sites in square pyramidal configuration Cu ²⁺ sites in square planar configuration
4	K ⁺ -NO	v(NO)	1886 1874	Unstable upon evacuation at 100 K
5	<i>cis</i> -(N ₂ O ₂)	v _s (NO) v _{as} (NO)	1863 1770	Weakly adsorbed in the zeolite channels, unstable upon evacuation at 100 K
6	N ₂ O	v(N-N)	2245	Weakly bonded in zeolite channels, unstable upon evacuation at 100 K
7	N ₂ O ₄ /NO ₂	v _{as} (NO ₂)	1683 1712 1749	Weakly bonded in zeolite channels, unstable upon evacuation at 100 K

UV-Vis characterization of copper containing zeolite samples

The self-supported pellets of the Cu²⁺-LTL sample pre-treated in O₂ and the Cu⁰-LTL sample pretreated in vacuum have been examined using diffuse reflectance UV-Vis spectroscopy (Figure 7). The Cu²⁺-LTL sample contains absorption bands in the regions 240 – 450 nm and 600 – 800 nm, that are described in the literature as mononuclear Cu²⁺ ← O²⁻ charge-transfer transitions and d – d transitions of isolated distorted octahedral Cu²⁺ ions, respectively.^{21,31} The presence of metallic copper species in the Cu⁰-LTL sample was revealed by an absorption peak at about 550 nm, which is attributed to surface plasmon polarization (SPP) resonance of the metallic Cu.^{31,32} This sample also shows band at 240 nm that is already assigned to Cu²⁺ species. Additional transitions at 360 nm belongs to O-Cu-O, and at 430 nm belongs to Cu-O-Cu complexes are recorded.³³

EPR characterization of copper containing zeolites

EPR spectroscopy characterizes the content of paramagnetic Cu^{2+} cations and changes in their local environment, while other copper oxidation states (Cu^+ , Cu^0) are EPR silent.³⁴

Figure 8 shows a drastic decrease in the amount of Cu^{2+} species upon reduction and partial re-oxidation upon calcinations in air.

Rasia et al. have shown the correlation between hyperfine coupling constant $A_{//}$ and g-factor ($g_{//}$) in the EPR spectra of Cu(II) complexes.³⁵

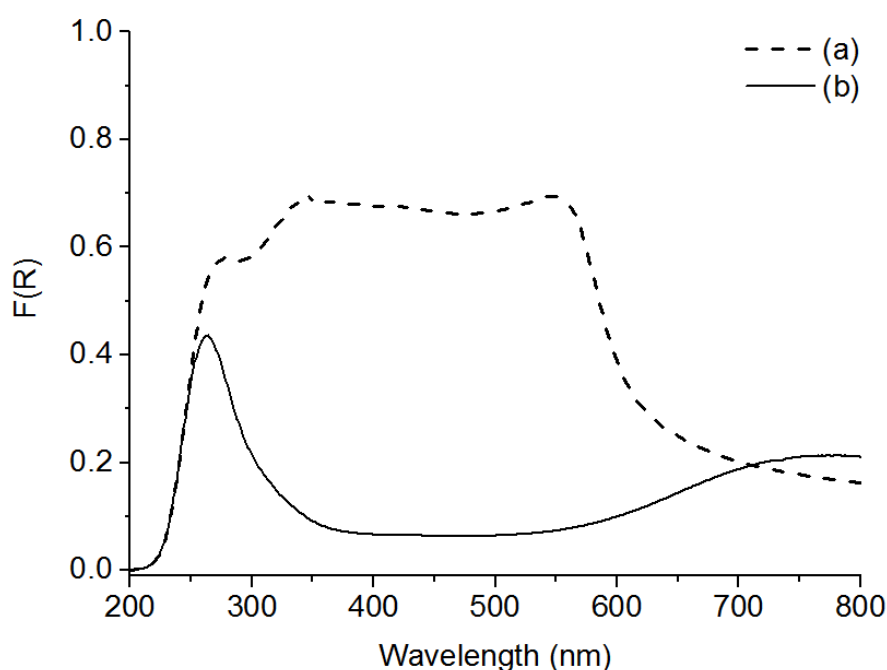


Figure 7 UV-Vis spectra of self-supported pellets of (a) Cu^0 -LTL and (b) Cu^{2+} -LTL activated under oxygen atmosphere at 673K

Table 4 The values of hyperfine coupling constant $A_{//}$ and g-factor ($g_{//}$) obtained for copper containing LTL samples from EPR spectra

Sample	Spin Hamiltonian Parameters	
	$g_{//}$	$A_{//}$
Cu^{2+} -LTL	2.4	132
Cu^0 -LTL	2.27	177
Cu^0 -LTL-reox	2.39	130

The dependence of these parameters allows determining the type of ligands coordinated to Cu^{2+} ions at different stages of preparation. The initial Cu^{2+} -LTL sample contains copper coordinated to four oxygen atoms, while after reduction the unreduced copper species are coordinated to the sphere of mixed ligands of nitrogen from hydrazine and oxygen. The above observations are in good agreement with previous reports, where Cu^{2+} closely interacts with four framework oxygen atoms in the 6MR's rings of copper-containing erionite, LTL Y, and CHA-zeolites.³⁶

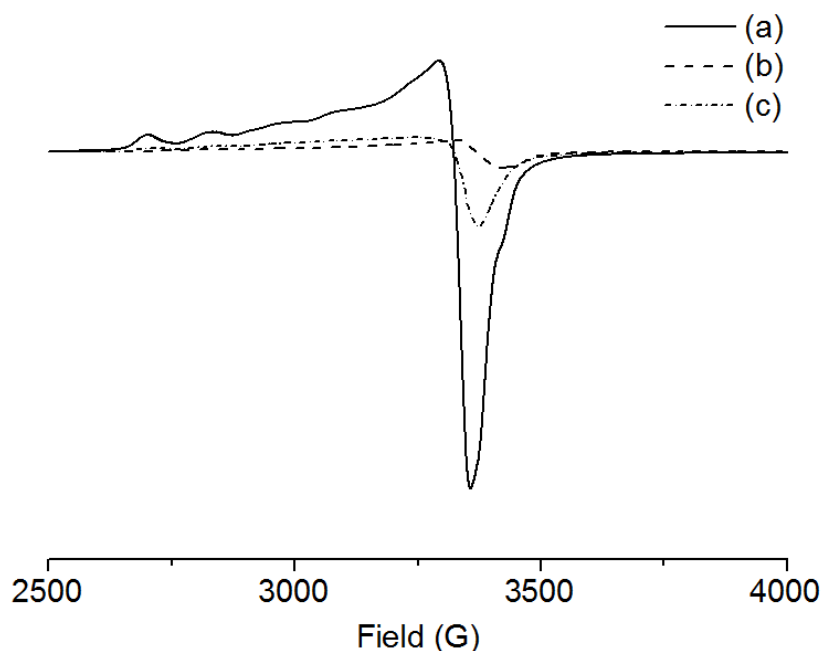


Figure 8 EPR spectra of (a) Cu^{2+} -LTL sample, (b) Cu^0 -LTL sample obtained by treatment with hydrazine and (c) Cu^0 -LTL sample upon thermal treatment in air

^{29}Si and ^{63}Cu MAS NMR characterization of copper containing zeolites

Due to a lower natural abundance of 4.7% and a long spin-lattice relaxation time (T_1) of ^{29}Si nuclei, the ^{29}Si MAS NMR measurements of porous silicates require long measuring time. While T_1 varies from a few microseconds to around 30 s for most of the zeolites, it can reach 5000 seconds in layered silicate nacrite.³⁷ However, it has been shown previously, that introducing paramagnetic centres into mesoporous and microporous silicate crystals has strong impact on shortening of the relaxation times due to effective nuclear relaxation by

direct interaction between the ^{29}Si nucleus and the electron spin.^{37,38} Hence, the measurement of the relaxation rate changes in ^{29}Si MAS NMR signal of copper-containing LTL zeolite allows monitoring the effective reduction of Cu^{2+} cations.

The ^{29}Si MAS spectra of parent LTL, Cu^{2+} -LTL and Cu^0 -LTL samples are shown in Figure 9. Four peaks at -90, -96, -101, and -106 ppm are assigned to $\text{Si}(0\text{Si}4\text{Al})$, $\text{Si}(1\text{Si}3\text{Al})$, $\text{Si}(2\text{Si}2\text{Al})$, $\text{Si}(3\text{Si}1\text{Al})$, $\text{Si}(4\text{Si}0\text{Al})$, respectively.³⁹ The T1 values for different sites in the parent LTL and copper-containing zeolites are summarized in Table 5. As can be seen, ^{29}Si T1 values of different silica sites in the parent zeolite are in the range of 9-12 s, while after the introduction of 1 paramagnetic Cu^{2+} ion per unit cell, the relaxation rate decreases drastically. It is worth noticing, that based on T1 values analysis of different Si sites, the preferable coordination of Cu^{2+} is revealed. The enhancement of relaxation time follows the order $\text{Si}(4\text{Al}) > \text{Si}(3\text{Al}) > \text{Si}(2\text{Al}) \geq \text{Si}(1\text{Al}) \geq \text{Si}(0\text{Al})$, suggesting that the most favourable coordination sites for Cu^{2+} species are $\text{Si}(4\text{Al})$ and $\text{Si}(3\text{Al})$. After reduction, the relaxation times have the values of same order of magnitude as for the parent LTL. These results suggest significant reduction of the amount of paramagnetic Cu^{2+} species in the sample.

Table 5 Relaxation time (T1) of different Q_n sites in the parent LTL and copper containing LTL zeolite samples

Sites	T1(s)		
	Parent LTL	Cu^{2+} -LTL	Cu^0 -LTL
Q₄(4Al)	11.6	2.9×10^{-2}	23.3
Q₄(3Al)	10.0	5.5×10^{-2}	19.0
Q₄(2Al)	9.2	8.4×10^{-2}	13.9
Q₄(1Al)	9.2	9.2×10^{-2}	12.3
Q₄(0Al)	9.1	8.5×10^{-2}	12.0

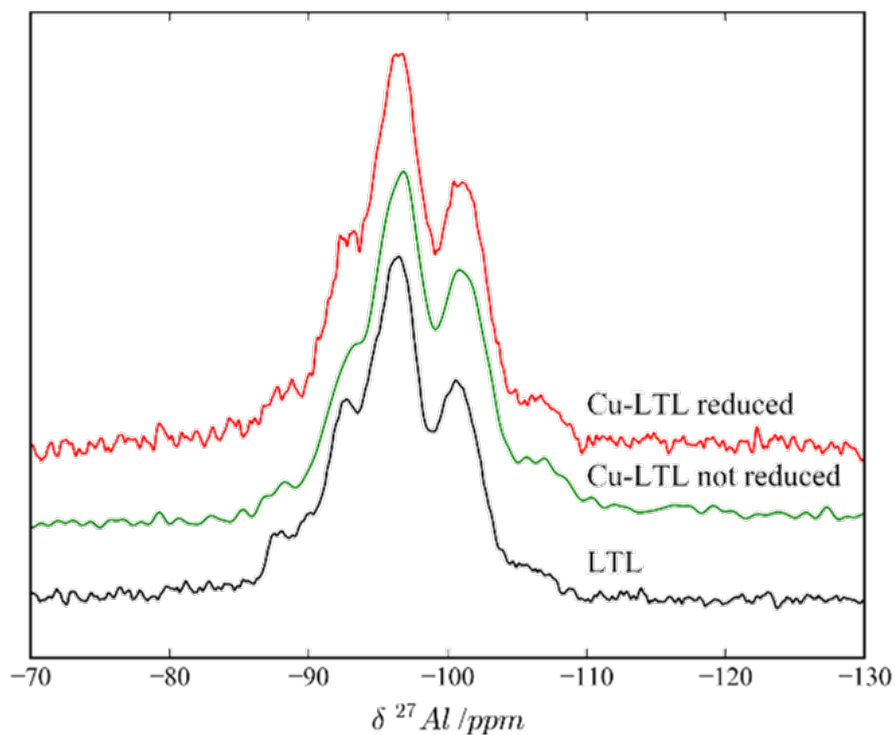


Figure 9 ^{29}Si MAS NMR spectra of parent LTL, Cu^{2+} -LTL and Cu^0 -LTL samples

The Cu^0 -LTL sample was then examined with ^{63}Cu MAS NMR. The anisotropic resonance at 2330 ppm prevails in the ^{63}Cu NMR spectra of parent LTL and Cu^{2+} -LTL samples, which arises due to the Cu radio frequency coil in the probe (Figure 10). No other signals are observed in these materials. Two extra resonances at 2340 ppm and 360 ppm are detected in the spectrum of the Cu^0 -LTL sample. The peak at 2340 ppm well-resolved from the peak of the Cu coil (at 2330 ppm) has been previously assigned to metal Cu particles.⁴⁰ Based on the FTIR study it was shown that the Cu^0 -LTL sample contains Cu^+ species that allows us to assign the peak at 360 ppm to Cu^+ .

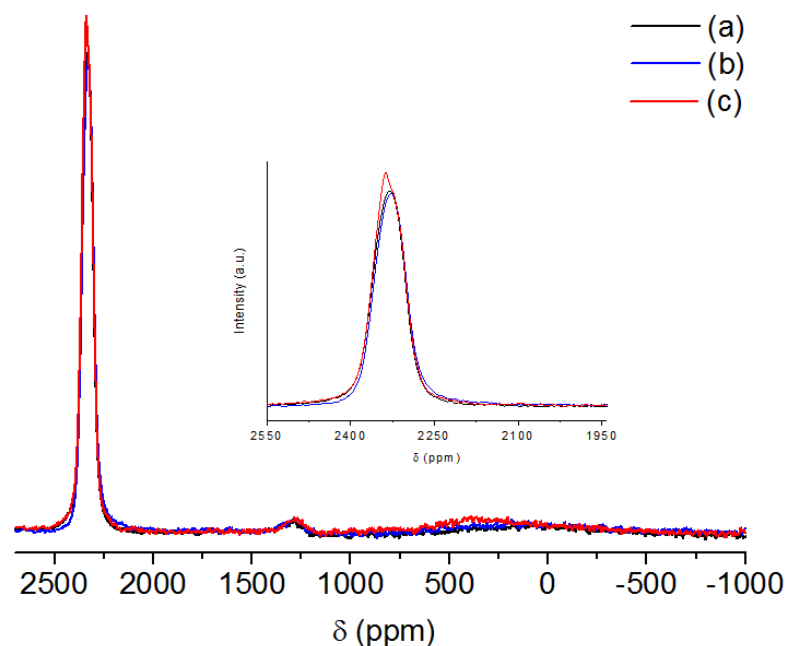


Figure 10 ^{63}Cu MAS NMR spectra of (a) parent LTL, (b) Cu^{2+} -LTL and (c) Cu^0 -LTL samples

Conclusions

The examination of oxidation states of supported copper species in LTL nanosized zeolites has been proved to be a demanding task, since the reduction of copper results in a complex system, containing different species including residuals of Cu^{2+} , Cu^+ , and CuNPs. Adsorption of probe molecules such as NO and CO allows monitoring of the modifications in the system upon oxidation and reduction; both the Cu^{2+} and Cu^+ were selectively probed. The FTIR results evidence the heterogeneity of Cu^{2+} and Cu^+ cations in the Cu-LTL zeolite prepared by ion-exchange procedure. Furthermore, the FTIR quantitative analysis based on CO adsorption shows that the relative amount of copper in (1+) state is 44%. This agrees with the UV-Vis results demonstrating that 56% CuNP were formed. The actual reduction of Cu^{2+} species and the presence of Cu^{2+} residuals (probably isolated ions) have been evidenced by adsorption of NO, as well as by complementary study using ^{29}Si MAS NMR and EPR. The ^{29}Si MAS spectra showed that the most favourable coordination sites for Cu^{2+} species are Si(4Al) and Si(3Al), whereas the ^{63}Cu MAS NMR confirms the presence of CuNPs.

References

- 1 W. Sheng, *Curr. Org. Chem.*, 2011, **15**, 3692–3705.
- 2 M. Hitrik, A. Dandapat, Y. Sasson, A. G. Livingston, K. K. Hii, G. Strukul, E. J. Mozeleski, D. W. Brown and E. M. Staudt, *RSC Adv.*, 2016, **6**, 68041–68048.
- 3 T. V. W. Janssens, H. Falsig, L. F. Lundegaard, P. N. R. Vennestrom, S. B. Rasmussen, P. G. Moses, F. Giordanino, E. Borfecchia, K. A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin and P. Beato, *ACS Catal.*, 2015, **5**, 2832–2845.
- 4 D. Farrusseng and A. Tuel, *New J. Chem.*, 2016, **40**, 3933–3949.
- 5 Y. Sun, *Chem. Soc. Rev.*, 2013, 2497–2511.
- 6 Y. Sun, *Mater. Today*, 2012, **15**, 140–147.
- 7 S. Wang, X. Huang, Y. He, H. Huang, Y. Wu, L. Hou, X. Liu, T. Yang, J. Zou and B. Huang, *Carbon N. Y.*, 2012, **50**, 2119–2125.
- 8 Y. Lu, W. Wei and W. Chen, *Chinese Sci. Bull.*, 2012, **57**, 41–47.
- 9 J. Kecht, Z. Tahri, V. De Waele, M. Mostafavi, S. Mintova and T. Bein, *Chem. Mater.*, 2006, **18**, 3373–3380.
- 10 J. Shi, Y. Wang, W. Yang, Y. Tang and Z. Xie, *Chem. Soc. Rev.*, 2015, **44**, 8877–8903.
- 11 S. Mintova, M. Jaber and V. Valtchev, *Chem. Soc. Rev.*, 2015, **44**, 7207–7233.
- 12 A. Kharchenko, O. I. Lebedev, V. Zholobenko, V. de Waele and S. Mintova, *J. Phys. Chem. C*, 2016, acs.jpcc.6b08045.
- 13 K. I. Hadjiivanov, *Adv. Catal.*, 2002, **47**, 307–511.
- 14 K. Hadjiivanov, *Catal. Rev.*, 2000, **42**, 71–144.
- 15 A. Vimont, F. Thibault-Starzyk and M. Daturi, *Chem. Soc. Rev.*, 2010, **39**, 4928–4950.
- 16 S. Bordiga, C. Lamberti, F. Bonino, A. Travert and F. Thibault-Starzyk, *Chem. Soc. Rev.*, 2015, **44**, 7262–7341.
- 17 C. Lamberti, A. Zecchina, E. Groppo and S. Bordiga, *Chem. Soc. Rev.*, 2010, **39**, 4951–5001.
- 18 G. T. Kerr, *J. Phys. Chem.*, 1969, **73**, 2780–2782.
- 19 K. Hadjiivanov and H. Knozinger, *Phys. Chem. Chem. Phys.*, 2001, **3**, 1132–1137.
- 20 J. Howard and J. M. Nicol, **5**.
- 21 A. Gallo, T. Tsoncheva, M. Marelli, M. Mihaylov, M. Dimitrov, V. Dal Santo and K. Hadjiivanov, *Appl. Catal. B Environ.*, 2012, **126**, 161–171.
- 22 G. Turnes Palomino, C. Otero Areán, F. Geobaldo, G. Ricchiardi, S. Bordiga and A. Zecchina, *J. Chem. Soc. Faraday Trans.*, 1997, **93**, 189–191.
- 23 E. Borfecchia, K. a. Lomachenko, F. Giordanino, H. Falsig, P. Beato, a. V. Soldatov, S. Bordiga and C. Lamberti, *Chem. Sci.*, 2014, **8**, 548–563.
- 24 G. . T. Palomino, P. Fisticaro, S. Bordiga, A. Zecchina, E. Giamello and C. Lamberti, *J. Phys. Chem. B*, 2000, **104**, 4064–4073.
- 25 V. Zdravkova, N. Drenchev, E. Ivanova, M. Mihaylov and K. Hadjiivanov, *J. Phys. Chem. C*, 2015, **119**, 15292–15302.
- 26 P. Kaminski, I. Sobczak, P. Decyk, M. Ziolek, W. J. Roth, B. Campo and M. Daturi, *J. Phys. Chem. C*, 2013, **117**, 2147–2159.
- 27 M. Tortorelli, K. Chakarova, L. Lisi and K. Hadjiivanov, *J. Catal.*, 2014, **309**, 376–385.
- 28 G. Centi and S. Perathoner, *Appl. Catal. A, Gen.*, 1995, **132**, 179–259.
- 29 I. Sobczak, M. Ziolek, M. Renn, P. Decyk, I. Nowak, M. Daturi and J. C. Lavalley, *Microporous Mesoporous Mater.*, 2004, **74**, 23–36.
- 30 A. Penkova, K. Hadjiivanov, M. Mihaylov, M. Daturi, J. Saussey and J.-C. Lavalley, *Lagmuir*, 2004, **20**, 5425–5431.
- 31 D. Esquivel, A. J. Cruz-Cabeza, C. Jiménez-Sanchidrián and F. J. Romero-Salguero,

- Microporous Mesoporous Mater.*, 2013, **179**, 30–39.
- 32 U. Kreibig, M. Quinten and D. Schoenauer, *Optical Properties of Nanoparticle Systems*, 1986, vol. T13.
- 33 A. N. Pestryakov, V. P. Petranovskii, A. Kryazhov, O. Ozhereliev, N. Pfander and A. Knop-Gericke, *Chem. Phys. Lett.*, 2004, **385**, 173–176.
- 34 U. Deka, I. Lezcano-Gonzalez, B. M. Weckhuysen and A. M. Beale, *ACS Catal.*, 2013, **3**, 413–427.
- 35 R. M. Rasia, C. W. Bertoncini, D. Marsh, W. Hoyer, D. Cherny, M. Zweckstetter, C. Griesinger, T. M. Jovin and C. O. Fernández, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 4294–4299.
- 36 R. a. Schoonheydt, *Catal. Rev. Sci. Eng.*, 1993, **35**, 129–168.
- 37 S. Inagaki, I. Kawamura, Y. Sasaki, K. Yoshida, Y. Kubota and A. Naito, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13523–13531.
- 38 L. Zhou, S. Li, Y. Su, B. Li and F. Deng, *Solid State Nucl. Magn. Reson.*, 2015, **66–67**, 29–32.
- 39 L. Mafra, J. A. Vidal-Moya and T. Blasco, *Annual Reports on NMR Spectroscopy*, 2012, vol. 77.
- 40 N. Yamakawa, M. Jiang and C. P. Grey, *Chem. Mater.*, 2009, **21**, 3162–3176.

Chapter 3

Cu species introduced in nanosized LTL zeolites by in-situ and ion-exchange approaches

Introduction

Isomorphous substitution of Si^{4+} cations in the silicon-oxygen skeleton of silicates and zeolites by transition metal cations M^{n+} with $n \neq 4$ is of great interest due to potentially imparted capacity for acid-base catalytic activity. Ione et al. systematically studied the problem of isomorphous substitution $\text{Si}^{4+} \rightleftharpoons \text{M}^{n+}$, and the stability of the M^{n+} in the tetrahedral position by applying the Pauling criteria was evaluated ($\rho = r_c/r_o$, where r_c is the cation radius and r_o is the radius of the oxygen ion).^{1,2} Based on the values of ρ , the tetrahedral coordination should be stable only for cations with ρ in the range 0.414–0.225. This group of cations includes only Al^{3+} , Mn^{4+} , Ge^{4+} , V^{4+} , Cr^{6+} , Si^{4+} , P^{5+} , Se^{6+} and Be^{2+} . However, it was shown later that any cation, that does not satisfy the rule above could be occluded in the isomorphous position at low concentration of the metal, the importance of geometrical parameters can be neglected.³

The aim of this work is to study the possibility of introducing copper in nanosized LTL zeolites by in-situ and ion exchange approaches and to follow the changes in their textural, structural, and surface properties.

Experimental

Materials

Aluminum hydroxide (reagent grade, Sigma-Aldrich), LUDOX[®] SM colloidal silica (30 wt. % suspension in H_2O , Sigma-Aldrich), potassium hydroxide (ACS reagent, $\geq 85\%$, pellets, Sigma-Aldrich), copper(II) nitrate trihydrate (puriss. p.a., 99-104%, Sigma-Aldrich), ammonium hydroxide solution (28%, Prolabo) were used as received.

In-situ synthesis of copper-containing LTL zeolite nanocrystals

Copper-containing zeolite nanocrystals with LTL-type structure were prepared from clear precursor suspension, free of organic template, forming a suspension with the following molar composition: 5 K₂O : 10 SiO₂ : 0.5 Al₂O₃ : 0.1 CuO : 200 H₂O. The suspension was prepared using the following procedure: solution A was prepared by dissolving 0.49 g of aluminum hydroxide and 2.5 g of potassium hydroxide in 4.2 g of distilled water to give a clear suspension; solution B was prepared by adding 10 g of colloidal silica and 0.8 g of potassium hydroxide in 4 g of distilled water and stirred until transparent; and solution C was prepared by mixing 1.2 g of copper (II) nitrate with 2 g of distilled water and 0.34 mL of ammonium hydroxide solution. Then, solution A was mixed with solution C, and the resulted mixture was poured slowly into solution B under vigorously stirring. The resulted gel (Figure 1) was aged for 60 h at room temperature under vigorous stirring till the bluish colloidal suspension was obtained. Then bluish colloidal suspension was subjected to hydrothermal treatment at 170 °C for 18 h. After the crystallization process was terminated, the nanosized zeolite crystals were recovered by multistep centrifugation (20000 rpm, 40 min) and washed with doubly distilled water until pH = 7 (sample K-Cu-LTL IS). To obtain the NH₄⁺-form of the K-Cu-LTL IS zeolite, the following three – step ion exchange procedure with ammonium chlorate at 40 °C was performed, followed by purification of the material by multistep centrifugation (20000 rpm, 40 min); this sample was named H-Cu-LTL IS.



Figure 1 The image of the synthesis gel after 60 h of aging (left) and after hydrothermal crystallization (right)

Ion-exchanged copper-containing LTL zeolite nanocrystals

The ion exchange LTL sample with copper was prepared following the procedure described in Chapter 2. The Cu^{2+} -LTL sample obtained by ion exchange treatment, that was thoroughly characterized in the Chapters 2 and 3, was named Cu-LTL IE here for the convenience.

Characterization

The crystalline structure of the samples was studied by using a *PANalytical* X'Pert Pro diffractometer with Cu $K\alpha$ monochromatized radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned in the range $3\text{--}80^\circ$ with a step size of 0.02° .

The agglomeration and average size of particles aggregates in the crystalline product were determined using dynamic light scattering (DLS) performed with a Malvern Zetasizer Nano instrument (scattering angle of 173° , laser wavelength of 632.8 nm , output power of 3 mW).

The surface and textural properties of the materials were measured by nitrogen sorption/desorption. Nitrogen adsorption/desorption isotherms were obtained using a Micrometrics ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 300°C under vacuum overnight prior to the measurement. The external surface area and micropore volume were estimated by alpha-plot method using Silica-1000 ($22.1 \text{ m}^2 \text{ g}^{-1}$ assumed) as a reference. The micropore and mesopore size distributions of the samples were determined from

the adsorption branch by the Nonlocal Density Functional Theory (NLDFT) and from the desorption branch using the Barret-Joyner-Halenda (BJH) algorithm, respectively.

Chemical composition of the zeolite powders was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian ICP-OES 720-ES.

The copper sites were studied by variable temperature pulsed EPR carried out at X-band (9.64 GHz) using a Brüker ELEXSYS E580 FT spectrometer. ^{63}Cu and ^{29}Si MAS NMR spectra were recorded by a Brüker 500 MHz spectrometer.

Additionally, *in situ* study of adsorption of probe molecules (NO, CO) on copper containing zeolite samples was performed. The FTIR spectra of self-supported zeolite pellets ($d = 16$ mm, $m = 20$ mg) were recorded using a Thermo-Nicolet Nexus instrument in an *in situ* transmission cell both at standard temperature (298 K) and at 100 K. Prior to the IR measurements, the samples were activated under oxygen atmosphere or in vacuum at 673 – 723 K, in order to study different copper species.

The state of copper was also characterized by diffuse reflectance UV-vis spectroscopy utilizing a Varian Cary 4000 spectrophotometer under ambient conditions (room temperature, air) and under heating up to 623 K in argon flow; the UV-vis spectra were plotted using the Kubelka–Munk function.

The X-ray photoelectron (XPS) measurements were carried out on an ESCALAB Mk II (VG Scientific) electron spectrometer (base vacuum of 10^{-8} Pa). XPS spectra were recorded using electron spectrometer equipped with a twin Mg/Al anode X-ray source and the instrumental resolution was of 1.06 and 1.18 eV for Mg $K\alpha$ and Al $K\alpha$ excitation sources, respectively. The energy scale was corrected with respect to the C1s - peak maximum at 285.0 eV for electrostatic charging. The processing of the measured spectra included a subtraction of X-ray satellites and Shirley-type background. The peak positions and areas were evaluated by a symmetrical Gaussian-Lorentzian curve fitting. The relative concentrations of the different species were

determined by normalization of the peak areas in regard to their photoionization cross-sections calculated by Scofield.^{4,5}

Results and discussion

The copper containing LTL nanosized zeolite (K-Cu-LTL IS) is prepared via a template-free synthesis route. The XRD patterns indicate that the K-Cu-LTL IS sample exhibits typical peaks associated with the LTL zeolite structure (Figure 2).⁶ It should be noted, that either CuO (35.5° and 38.6° 2θ) or Cu₂O (36.44° 2θ) phases are not detected in the XRD pattern of the K-Cu-LTL IS.⁷ The influence of the copper introduced by in situ and ion exchange approaches on the change of the unit cell parameters of the as-prepared hydrated samples was evaluated by applying the Pawley fit (see Chapter 2). The unit cell parameters of parent LTL, K-Cu-LTL IS and K-Cu-LTL IE samples are presented in Table 1.

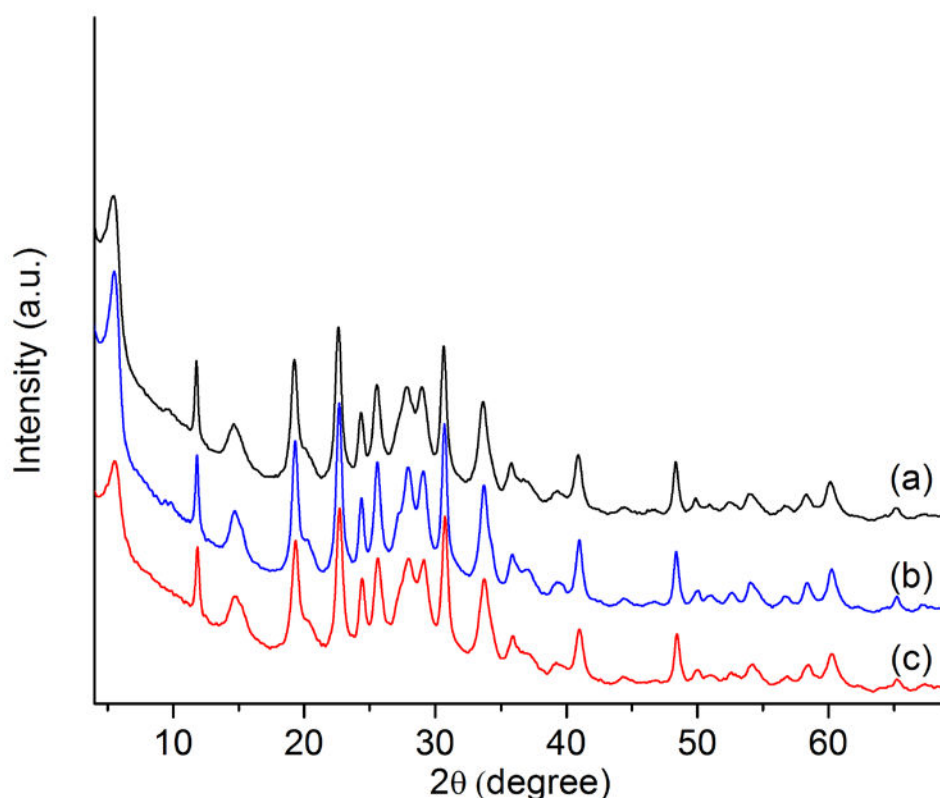


Figure 2 XRD patterns of (a) parent LTL, (b) K-Cu-LTL IE and (c) K-Cu-LTL IS samples.

Table 1 Unit cell parameters of samples and size of the crystals determined by Pawley fit using X'Pert HighScore Plus software

Sample	a = b, Å	c, Å	V, Å ³	Size, nm*
Parent LTL	18.372990	7.540921	2204.523	11
K-Cu-LTL IE	18.374080	7.544786	2205.916	11
K-Cu-LTL IS	18.359850	7.533496	2199.205	15

*Obtained from the X'Pert HighScore Plus software, that used Scherrer algorithm

It is known from the literature, that the incorporation of metal cations with ionic radius distinct from Si^{4+} and Al^{3+} can affect the unit cell parameter.⁸ Table 1 reveals the moderate expansion of the unit cell parameters in the K-Cu-LTL IE sample. On the contrary, a contraction of the unit cell parameters for sample K-Cu-LTL IS is observed. Since the effective ionic radius of

Cu^{2+} (0.062 nm for coordination number IV) is larger than those of Si^{4+} (0.026 nm for coordination number IV) and Al^{3+} (0.039 nm for coordination number IV),⁹ one would expect the expansion of the unit cell in case of the incorporation of Cu ions into the framework sites of the LTL type zeolite structure (K-Cu-LTL IS). While in the case of copper introduction via ion exchange, the smaller Cu^{2+} ion (0.062 nm) substitutes K^+ with larger ionic radius (0.138 nm). In earlier papers, it has been found, that the hydration of the zeolites influences the unit cell parameters and more specifically FAU type zeolite was considered.¹⁰ Therefore, thermogravimetical analysis (TG) of the hydrated samples were performed. The TG curves show similar shapes, the weight loss below 180 °C corresponds to the water removal from the zeolite structure (Figure 3).¹¹ The weight loss of the K-Cu-LTL IE sample is higher (18 %) than for the K-Cu-LTL IS (13 %), which indicates higher hydrophobicity of the K-Cu-LTL IE in comparison to parent LTL and K-Cu-LTL IS samples. This could explain the increase in the unit cell parameters of the ion exchanged K-Cu-LTL IS sample.

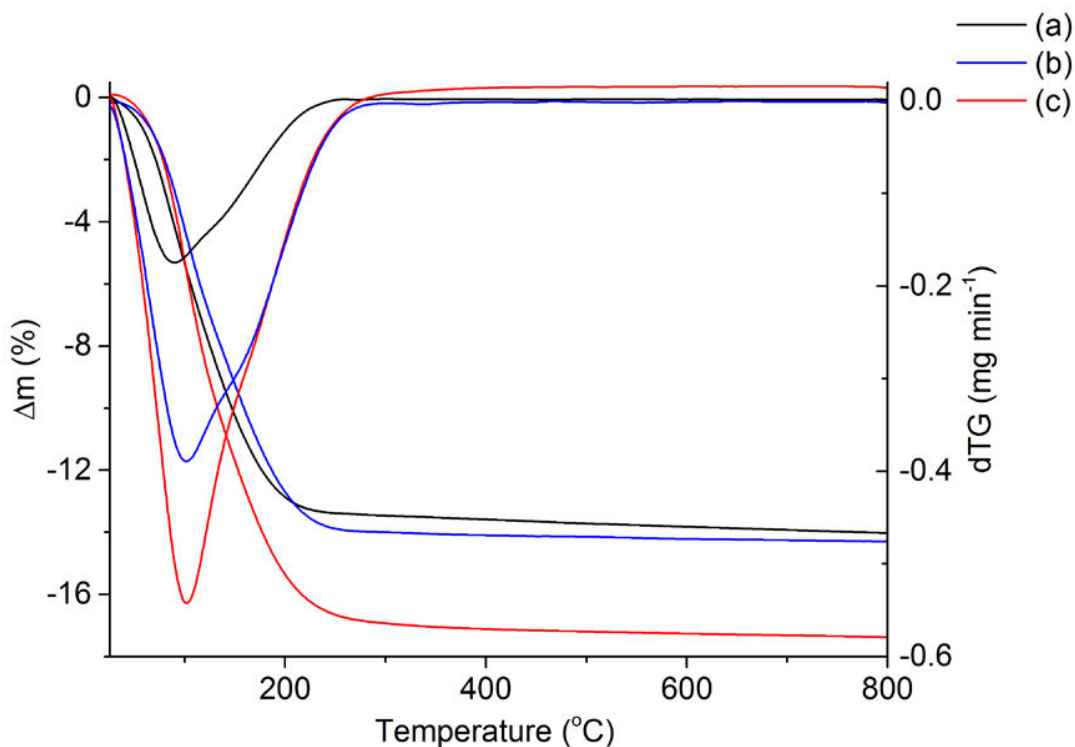


Figure 3 TG/DTG curves for (a) parent LTL, (b) K-Cu-LTL IE and (c) K-Cu-LTL IS samples

Copper complexes are known in oxidation states ranging from 0 to 4+, however the most common are the 2+ (cupric) and the 1+ (cuprous) oxidation states, with the divalent state prevailing. The coordination numbers and geometries of copper complexes vary with oxidation state. Thus, the majority of the characterized Cu (III) complexes are square planar and diamagnetic, for the spherically symmetric Cu (I) d^{10} ion; the common geometries are two-coordinate linear, three-coordinate trigonal planar, and four-coordinate tetrahedral. Some distortions from these ideal geometries are observed, particularly with chelating ligands. The d^9 Cu (II) ion is commonly found in a tetragonal coordination environment, with four shorter equatorial bonds and another one or two longer axial bonds and less often with two shorter axial bonds and four longer equatorial bonds. Four-coordinate tetrahedral and planar complexes are also known, for instance, the CuCl_4^{2-} ion, which crystallized in geometries ranging from square planar (usually green) to almost ideal tetrahedral (usually orange).

Additionally, five-coordinate trigonal bipyramidal to square-planar complexes have been reported.¹² The Cu (II) oxides M_2CuO_3 ($M = Ba, Sr$) contain linked CuO_4 planar units. The crystal structures of some pyrophosphate-containing compounds comprise square-planar CuO_4 units in open-framework structures. Also square planar, trigonal bipyramidal, and distorted octahedral geometries are found for the copper ions in mixed strontium-copper phosphate structures.¹² It has been emphasized, that oxides containing transition metal ions with partially filled e_g orbitals like Cu^{2+} will undergo strong Jahn-Teller (JT) distortion.¹³ From the above considerations, the Cu – O – Cu angles and Cu – O bond distances will be affected by the environment of the copper, which in turn could affect the unit cell parameter of the materials (in our case zeolite) and lead to its diminution, as it has been shown for substitution of Si by Al.^{14,15}

The porosity of the samples was analyzed by N_2 sorption (Figure 4). The N_2 sorption isotherm of the K-Cu-LTL IS sample exhibits mixed type I and IV with a sharp uptake at low relative pressure and a slowly increasing one at higher relative pressure, similar to the ones observed for parent LTL and K-Cu- LTL IE samples, which are typical for micro/mesoporous materials.

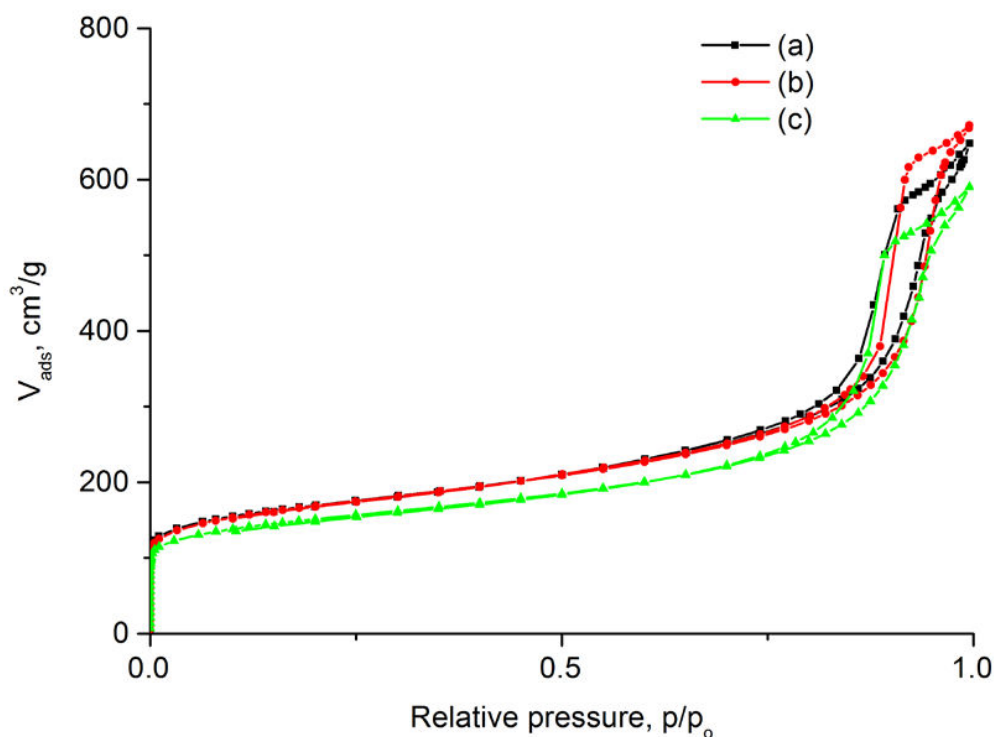


Figure 4 Nitrogen adsorption/desorption isotherms of (a) parent LTL, (b) K-Cu- LTL IE and (c) K-Cu-LTL IS samples

Table 2 BET surface area (S_{BET}), micro- (V_{mic}), meso- (V_{meso}) and total (V_{tot}) pore volumes of parent LTL, K-Cu- LTL IE and K-Cu-LTL IS samples

Sample	S_{BET} , $\text{m}^2 \text{g}^{-1}$	V_{mic} , $\text{cm}^3 \text{g}^{-1}$	V_{tot} , $\text{cm}^3 \text{g}^{-1}$	V_{mes} , $\text{cm}^3 \text{g}^{-1}$
Parent LTL	571.4	0.12	1.00	0.88
K-Cu-LTL IE	571.9	0.11	1.04	0.93
K-Cu-LTL IS	511.4	0.11	0.91	0.80

As can be seen from the Table 2, all samples show a large BET surface area and pore volume, suggesting the existence of abundant open pores. Compared to parent material and the material obtained via ion exchange, the K-Cu-LTL IS samples demonstrate a slight decrease in the BET surface area which is probably due to the negligible change in the particle size distribution. Indeed, according to the XRD results, the size of the crystallites in the K-Cu-LTL IS sample is slightly larger in comparison to the other two samples (Table 1). The size of the parent LTL

crystals is 11 nm, and reaches 15 nm when Cu is introduced by in situ approach (sample K-Cu-LTL IS). In addition, the pore blockage does not take place, since the samples do not demonstrate a decrease in the micropore volume neither for K-Cu-LTL IS nor K-Cu-LTL IE.

The chemical composition of all samples as prepared (LTL, K-Cu-LTL IE, K-Cu-LTL IS) and in proton form (H-Cu-LTL IS) measured by ICP-OES and EDX is presented in Table 3.

Table 3 Chemical composition of samples measured by ICP-OES and EDX (the elemental ratios are obtained from the atomic percent of the elements)

Sample	ICP-OES			EDX		
	Si/Al	K/Al	Cu/Al	Si/Al	K/Al	Cu/Al
Parent LTL	2.90	2.18	-	2.46	0.89	-
K-Cu-LTL IE	2.83	1.37	0.06	2.59	0.82	0.12
K-Cu-LTL IS	2.91	1.99	0.07	2.60	0.95	0.08
H-Cu-LTL IS	-	-	-	2.56	0.36	0.08

As can be seen, the amount of copper in both series of experiments is similar, that allows further comparison of the copper species in the zeolite crystals obtained via ion exchange and in situ synthesis approaches. The amount of copper introduced in the samples corresponds to one copper atom per unit cell of LTL crystals, though the silicon to aluminum ratio Si/Al is not expected to change significantly with incorporation of Cu species in the framework. Interestingly, the chemical analysis of the sample after NH₄Cl ion exchange (H-Cu-LTL IS) indicates that only K⁺ ions have been eliminated.

It is well known, that the UV-vis spectroscopy is sensitive to the oxidation state and coordination of metals.^{16–18} Electronic spectra analysis involving d–d transitions is possible only for Cu²⁺ (3d⁹) systems, since Cu⁺ ion has a fully occupied d shell (3d¹⁰).¹⁹ For copper, the following transitions should be noted in the UV-vis spectral range (Table 4).¹⁸

Table 4 Assignments of the DRS adsorption maxima of copper compounds (adapted from [12])

Absorption range	Nature of transitions	Symmetry (valency)
16670-12500 cm ⁻¹	d-d of Cu ²⁺	Octahedral (~tetragonally distorted)
13500-12500 cm ⁻¹	d-d of Cu ²⁺	Octahedral
16670 cm ⁻¹	d-d of Cu ²⁺	Strong distortion (nearly square planar)
11765-11111 cm ⁻¹	d-d of Cu ²⁺	Square pyramid
10000-5880 cm ⁻¹	d-d of Cu ²⁺	Tetrahedral
25000-22222 cm ⁻¹	Emission/adsorption of a photon	Cu ⁺ three-dimensional clusters in CuO
44444-16949 (edge at 17241-16949) cm ⁻¹	Conduction band	Metallic Cu ⁰
40000-35714, 32258 and 28571 cm ⁻¹	Charge transfer O ²⁻ → Cu ²⁺	Cu ²⁺
31250 and 22727 cm ⁻¹	Charge transfer	Cu ²⁺ -O ²⁻ -Cu ²⁺
UV up to 31250 cm ⁻¹	d ¹⁰ -d ⁹ s ¹ (d ¹⁰ 4s-d ¹⁰ 4p)	Cu ⁺ (Cu ⁰)
15385 nm	d-d of Cu ²⁺	Distorted octahedral (square planar)

The diffuse reflectance UV-vis spectra of the samples before and after dehydration under Ag flow at 623 K are depicted in Figure 5. Several signals in the UV-vis spectra of the samples reveal the existence of various copper species. The strong band at ~38460 cm⁻¹ is assigned to charge transfer transitions from oxygen in the zeolite crystal lattice O²⁻ to isolated copper ion Cu²⁺ (O²⁻ → Cu²⁺), suggesting the existence of mononuclear Cu²⁺ ions in both ion exchanged (K-Cu-LTL IE) and in situ (K-Cu-LTL IE) prepared samples, while this signal is absent in the parent LTL material. The K-Cu-LTL IE additionally exhibits broad adsorption band between 33333 and 16670 cm⁻¹. It has been reported, that Al sites distribution in the material affects the concentration and the type of the hydrated Cu²⁺ complexes presented in the Cu-exchanged SSZ-13: (i) divalent complexes charge compensated by a pair of nearby Al, e.g. [Cu(H₂O)₆]²⁺ or [Cu-O(L)_{6-n}(H₂O)_n]²⁺ (where O(L) are oxygen framework atoms coordinated to Cu²⁺); (ii) “monovalent” complexes charge compensated by one Al atom, e.g. [Cu-OH(H₂O)₅]⁺ or [Cu-(OH)O(L)_{5-n}(H₂O)_n]⁺.¹⁹ Hence, the presence of one or more ligands with different

electronegativity (e.g. OH^- , framework oxygen) yield in a more distorted site and in a shift of the absorption band to higher frequencies.¹⁹ Even though, the band is too broad to discriminate the co-presence of the transitions of different species, the observed band might be assigned to some Cu^+ clusters or oligomeric species $[\text{Cu}^{2+}\text{-O}^{2-}\text{-Cu}^{2+}]$, or most probably to hydrated distorted square planar Cu^{2+} , since after dehydration at 623 K this broad band disappears, and copper species change their coordination to octahedral or distorted octahedral coordination (transition at 12500 cm^{-1}). This can be explained with a tendency of Cu^{2+} to migrate inside the zeolite cavities and lose the ligands upon heating, which is in agreement with previous reports.^{18,20} Unlike ion-exchanged sample, the K-Cu-LTL IS sample displays a tail peak around 31642 cm^{-1} that emerges before and after dehydration at 623 K, suggesting the presence of $[\text{Cu}^{2+}\text{-O}^{2-}\text{-Cu}^{2+}]$ that are stable upon heating. Yet, no information can be extracted on the coordination of the isolated Cu^{2+} ions.

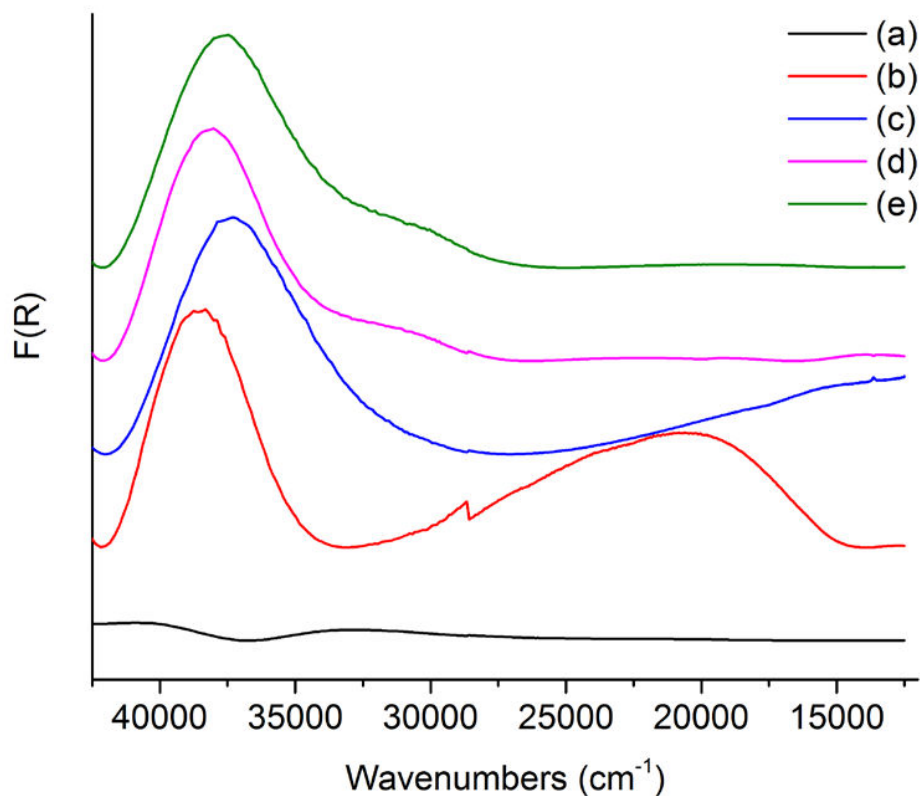


Figure 5 DR UV-vis spectra of (a) parent LTL, (b) K-Cu-LTL IE hydrated, (c) K-Cu-LTL IE dehydrated at 623 K, (d) K-Cu-LTL IS hydrated and (e) K-Cu-LTL IS dehydrated at 623 K samples

XPS was used to gain insight on the relation between distribution and environment of Cu sites and the synthesis procedure applied for the preparation of copper containing zeolite samples. In the literature, copper is characterized by the $2p_{3/2}$ level with an energy 932.5 ± 0.24 eV for copper (I), while for copper(II) these values are 933.57 ± 0.39 eV for oxides, and 934.75 ± 0.50 eV for hydroxides and the presence of high-energy shake-up satellites for 2p bands.^{5,21–24}

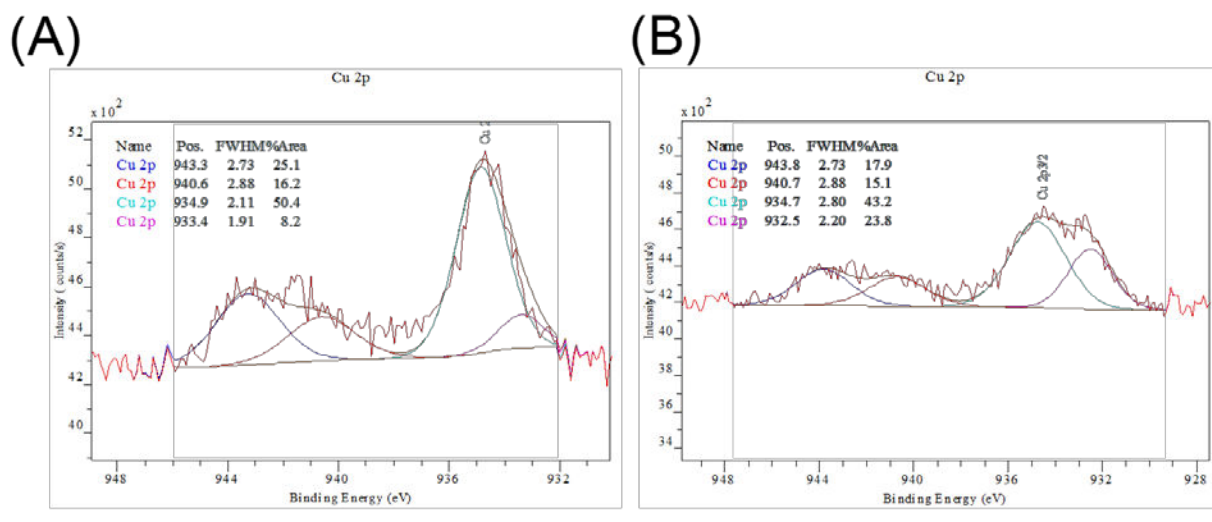


Figure 6 XPS spectra of (A) K-Cu-LTL IE and (B) K-Cu-LTL IS samples

Figure 6 shows a comparison between samples obtained by direct synthesis (K-Cu-LTL IS) and ion exchange (K-Cu-LTL IE) approaches. For the K-Cu-LTL IS sample, the Cu 2p_{3/2} band consists of two components: 934.9 eV (86%) and 933.4 eV (80%) with satellite features at about 943 eV. In case of the copper(I) valence state, an additional spectral component with a lower (about 932 eV) binding energy would appear. Accordingly, both high and low-energy spectral components have been assigned to two different types of Cu²⁺ with different environment.²⁴

The XPS spectrum of the K-Cu-LTL IE consists of two components: 934.7 eV (65%) and 932.5 eV (35%) with the satellite at about 943 eV, thus suggesting the existence of both Cu²⁺ and Cu⁺ species at the same time. The presence of Cu⁺ state in the hydrated sample can be explained by the partial reduction under long X-ray exposure or ion bombardment under ultrahigh vacuum conditions treatments.²⁵ In summary, the above results denote the occurrence of several types of Cu²⁺ species with different environment. Some occluded extra-framework Cu²⁺ species in the K-Cu-LTL IS sample, that could not be removed together with K⁺ during the exchange with NH₄Cl are seen. In the ion-exchanged sample (K-Cu-LTL IE) mainly isolated Cu²⁺ cations in different coordination, that can be easily reduced to Cu⁺ are measured.

Adsorption of CO probe molecule on copper containing samples study by FTIR spectroscopy

The distribution of copper species is also studied by adsorption of probe molecule (CO) on K-Cu-LTL IS and H-Cu-LTL IS samples. The IR spectra (C-O-stretching region) of the K-Cu-LTL IS sample are shown in Figure 7 (A, B). The CO adsorption spectra of both pre-treated in oxygen and in vacuum at 673 K for H-Cu-LTL IS sample are depicted in Figure 8 (A, B); CO stretching frequencies are summarized in the Tables 5 to 8. Various pretreatment conditions were used to monitor the changes of copper species occurring after exposing the sample to different atmosphere and after converting the material in NH_4^+ -form.

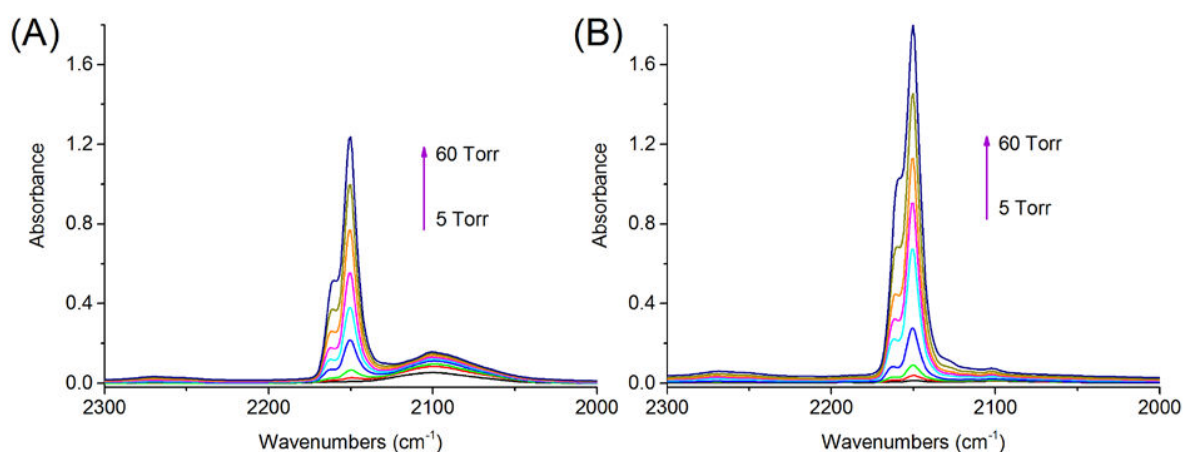


Figure 7 Evolution of the IR spectra in the 2300-2000 cm^{-1} range upon interaction with CO probe molecule (5-60 Torr) at 100 K. K-Cu-LTL IS sample activated at 673 K in vacuum (A) and activated at 673 K in O_2 (B)

Table 5 Assignment of C–O stretching frequencies observed for the K-Cu-LTL IS sample

No.	Species	Mode	Frequency, cm^{-1}	Notes
1	$\text{Cu}^+-(\text{CO})_2 / \text{K}^+-\text{CO}$	$\nu_{\text{as}}(\text{CO})$	2150	Appear at 100 K, unstable upon evacuation at RT
2	$\text{Cu}^+-\text{CO} / \text{K}^+-\text{CO}$	$\nu_{\text{s}}(\text{CO})$	2161	Appear at 100 K, unstable upon evacuation at RT
3	Cu^+-CO	$\nu(\text{CO})$	2128	Appear at 100 K, unstable upon evacuation at RT
4	$\text{Cu}^+-\text{CO} / \text{Cu}^0-\text{CO}$	$\nu(\text{CO})$	2103	Populated first at 100K, unstable upon evacuation at RT

Adsorption of CO (5 – 20 torr) on the K-Cu-LTL IS sample, activated under vacuum at 673 K, leads to the appearance of band at 2103 cm^{-1} , that can be presumably assigned to both $\text{Cu}^0\text{-CO}$ and $\text{Cu}^+\text{-CO}$ (Figure 7A). The bands at 2150 and 2163 cm^{-1} , that appear simultaneously and in the first approximation are assigned to C-O-stretching of $\text{K}^+\cdots\text{CO}$ adducts according to previous reports.²⁶ The IR spectra collected for K-Cu-LTL IS sample, activated at 673 K under oxygen at 673 K leads to the appearance of mainly the bands at 2150 and 2163 cm^{-1} (Figure 7B). High intensity of these bands in comparison to the results obtained under vacuum suggests that there is spectral overlapping of several different species. The intensity of the band at 2103 cm^{-1} decreases substantially after samples treatment under O_2 ; a peak shoulder at 2127 cm^{-1} is observed as well. Comparison of the results presented in Figures 7 A and B shows significant oxidation of copper in O_2 atmosphere. Zecchina et al. show that in the presence of pre-adsorbed Lewis bases, such as NH_3 , a downward shift of the $\nu(\text{CO})$ was observed.²⁷ Since ammonium hydroxide was used in the synthesis, it could be assumed that some residue could be still presented in the K-Cu-LTL IS sample. However, the initial IR spectrum of the K-Cu-LTL IS sample does not reveal a complex absorption in the 3500-3100 cm^{-1} range due to $\nu(\text{NH})$; a peak at 1610 cm^{-1} due to $\delta(\text{NH})$ is not present either.²⁷ In addition, the TG data reveals the weight loss attributed to the water only. On the other hand, the lower frequencies of CO coordinated to Cu^+ ions may be explained by the higher coordination of the latter when supported on oxides rather than on zeolites, that leads to a lower electrophilicity and a weaker σ bond with CO. Thus, the complexes are less stable and the frequency of adsorbed CO is at lower wavenumbers.²⁸ Indeed, reduced bulk CuO has been characterized by two bands at 2115-2100 cm^{-1} and 2135 cm^{-1} , while the $\text{Cu}^+\text{-CO}$ band for bulk Cu_2O has been found at 2127 cm^{-1} . The band at 2150 cm^{-1} , that appears at higher coverage, has been considered as an evidence of the formation of the $\text{Cu}^+\text{-(CO)}_2$ dicarbonyls. While the peak at 2160 cm^{-1} as previously found in zeolite CuY was assigned to $\text{Cu}^+\text{-CO}$ complexes.

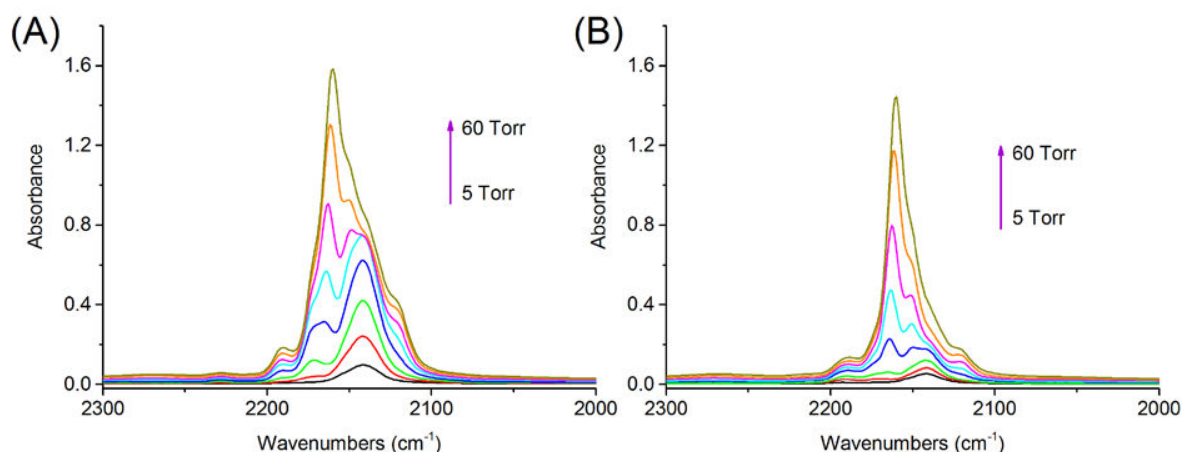


Figure 8 Evolution of the IR spectra of sample H-Cu-LTL IS in the 2300-2000 cm^{-1} range upon interaction with CO (5-60 Torr) at 100 K: sample activated at 673 K in vacuum (A) and O_2 (B).

Table 6 Assignment of the C–O stretching frequencies measured for the H-Cu-LTL IS sample.

No.	Species	Mode	Frequency, cm^{-1}	Notes
1	$\text{Cu}^+\text{-CO}$	$\nu(\text{CO})$	2140	Populated first, stable upon evacuation at RT
			2128	Populated first, stable upon evacuation at 423 K
			2160	
2	$\text{Cu}^+\text{-(CO)}_2$	$\nu_s(\text{CO})$ $\nu_{as}(\text{CO})$	2177	Appear at high coverages at 100 K, not stable upon evacuation
			2150	
3	$\text{Cu}^{2+}\text{-CO}$	$\nu(\text{CO})$	2190	Unstable upon evacuation at 100 K
4	$\text{K}^+\text{-CO}$	$\nu_s(\text{CO})$ $\nu_{as}(\text{CO})$	2163	Appears at higher coverages at 100 K, unstable upon evacuation
			2150	
5	OH-group	$\nu(\text{CO})$	2160	Interaction with silanol group
			2177	Interaction with bridging OH group
6	$\text{Al}^{3+}\text{-CO}$	$\nu(\text{CO})$	2230	Appears at 100 K, unstable upon evacuation

Figure 8 shows H-Cu-LTL IS sample pretreated at 673 K in vacuum and under oxygen atmosphere. The modification of the spectra in comparison to the K-Cu-LTL IS samples is evident. These two samples show identical spectral features as the K-Cu-LTL IE sample obtained via ion exchange approach; the bands at 2140 and 2128 cm^{-1} ($\text{Cu}^+\text{-CO}$) are the first to be populated. The first difference from the previous observations for the ion-exchanged sample is the intensity of the two bands at 2177 and 2163 cm^{-1} . The peak at 2177 cm^{-1} corresponds to

the interaction of CO with bridging OH-groups, thus confirming the success of the ion exchange with NH_4Cl .²⁸ Another important difference compared to K-Cu-LTL IE sample, is the lower intensity of the bands at 2140 and 2128 cm^{-1} ($\text{Cu}^+\text{-CO}$). It is worth reminding, that the amount of copper is the same in both samples obtained by in situ (K-Cu-LTL IS) and ion exchange (K-Cu-LTL IE) approaches. The results indicate a lower concentration of Cu^+ -species able to interact with CO in the K(H)-Cu-LTL IS sample.

Adsorption of NO probe molecule on copper containing samples study by FTIR spectroscopy

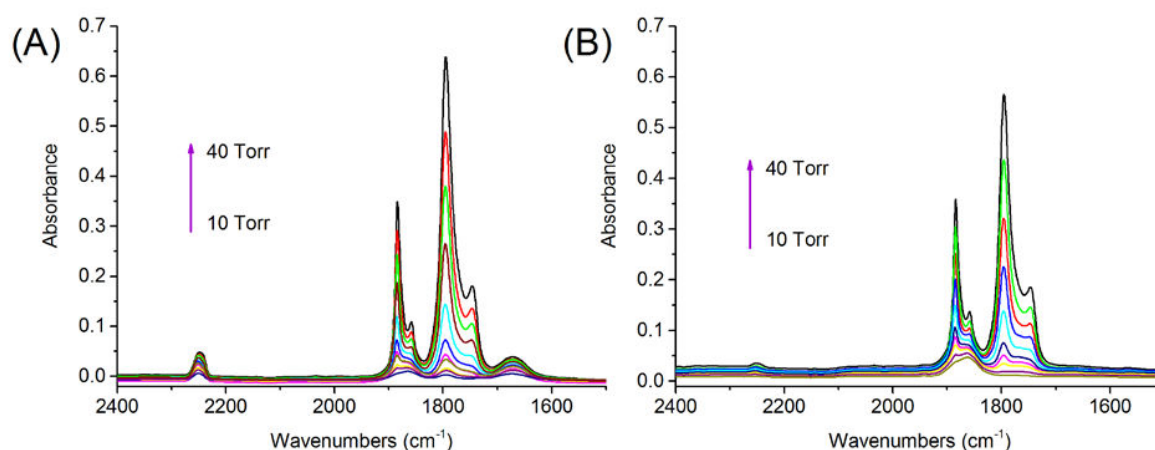


Figure 9 Evolution of the IR spectra of sample K-Cu-LTL IS in the 2400-1500 cm^{-1} range upon interaction with NO (10-40 Torr) at 100 K: sample activated at 673 K in vacuum (A) and O_2 (B).

Table 7 Assignment of the N–O stretching frequencies measured for the K-Cu-LTL IS sample.

No.	Species	Mode	Frequency, cm ⁻¹	Notes
1	Cu ⁺ -NO	v(NO)	1795	Two different Cu ²⁺ -sites on the CuO
2	Cu ²⁺ -NO	v(NO)	1858	
			1870	
			1884	Cu ²⁺ sites in square planar configuration Detected at 100 K, unstable upon evacuation
3	K ⁺ -NO	v(NO)	1870	
			1886	
4	N ₂ O	v(N-N)	2250	
5	NO ₂ /N ₂ O ₄	v _{as} (NO ₂)	1670	
			1746	

The NO adsorption of calibrated doses from 10 to 40 torr on the samples at low temperature was performed. The IR spectra for K-Cu-LTL IS sample is shown in Figure 9A, B.²⁹ The observed bands and their assignments are summarized in Table 7.

The K-Cu-LTL IS sample pretreated in vacuum at 673 K reveals several bands. The peaks at 1858 and 1870 cm⁻¹ are characteristic for Cu²⁺-NO species of CuO and correspond to two different Cu²⁺ sites. While the peak at 1884 cm⁻¹ corresponds to Cu²⁺ sites in square planar coordination.^{16,29,30} The second set of bands includes peaks at 1795 cm⁻¹ represents the interaction of NO with Cu⁺-sites.²⁹ One more peak shoulder centered at 1870 cm⁻¹ and 1886 cm⁻¹ has been assigned to the K⁺...NO monomers.³¹ The latter are masked in the case of the samples pretreated in O₂ or under vacuum. All four samples contain the peak at 2245 cm⁻¹, that has been previously described as weakly bonded N₂O with zeolites.³¹ The peaks centered at 1670 cm⁻¹ and 1746 cm⁻¹ have been attributed to N₂O₄ or NO₂, respectively. The presence of various N_xO_y in the spectra could be explained by NO disproportion or by the contamination of the NO.²⁹ It can be clearly observed, that the appearance of the latter bands strongly depends on the properties of the surface of the samples that are tailored during the pretreatment, but not on the contamination of NO. The bands at 2245 cm⁻¹ and 1680 cm⁻¹ disappear after interaction of the samples with oxygen at 673 K (Figure 9B). The main peaks are still present, however the bands assigned to Cu²⁺ species are of higher intensity, while the band at 1796 cm⁻¹ has lower intensity.

In general, the behavior of NO adsorption in the K-Cu-LTL IS samples follows the same trend as for CO adsorption, sustaining the presence of the CuO extra-framework species in the system.

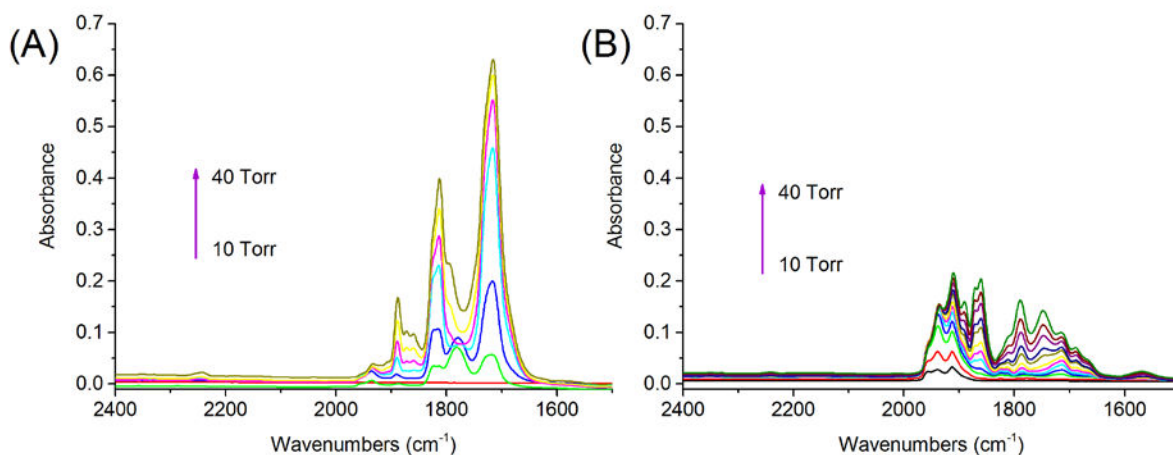


Figure 10 Evolution of the IR spectra of sample H-Cu-LTL IS in the 2400-1500 cm⁻¹ range upon interaction with NO (10-40 Torr) at 100 K activated at 673 K in vacuum (A) and O₂ (B).

Table 8 Assignment of the N–O stretching frequencies observed for the H-Cu-LTL IS sample.

No.	Species	Mode	Frequency, cm ⁻¹	Notes
1	Cu ⁺ -NO	v(NO)	1790	Converts to dinitrosyls, not stable upon evacuation
2	Cu ²⁺ -NO	v(NO)	1810	
3	Cu ²⁺ -NO	v(NO)	1910	Isolated Cu ²⁺ sites in square pyramidal configuration
			1936	
4	Cu ⁺ -(NO) ₂	v _s (NO)	1958	Correspond to associated Cu ²⁺ sites
			1858	
5	K ⁺ -NO	v(NO)	1870	Two different Cu ²⁺ -sites on the CuO
			1890	
6	N ₂ O ₄	v _{as} (NO ₂)	1747	Weakly adsorbed, unstable upon evacuation at 100 K
			1715	
7	NO ₂ or N ₂ O ₄	v _{as} (NO ₂)	1685	
8	Bridging nitrates	v ₃ (split mode)	1663	Extra- framework copper site
9	Bidentate nitrate	v ₃ (split mode)	1566, 1304	Adsorption on isolated copper–oxygen species
10	cis-(NO) ₂	v _s (NO)	1863	Weakly adsorbed in the zeolite channels, unstable upon evacuation at 100 K
		v _{as} (NO)	1778	
11	N ₂ O	v(N-N)	2245	Weakly bonded in zeolite channels, unstable upon evacuation at 100 K

Figure 10 shows the IR spectra collected for sample H-Cu-LTL IS pretreated at 673 K in vacuum and under oxygen atmosphere at 673 K. The change of the spectra in comparison to the K-Cu-LTL IS samples is noticeable. These two samples show identical to the K-Cu-LTL IE sample spectral features. The bands at 1953, 1938, 1905, 1886 cm^{-1} are characteristic for Cu^{2+} -NO species and correspond to four different Cu^{2+} sites. The second set of bands at 1825, 1810, 1797 and 1730 cm^{-1} generally represent the interaction of NO with Cu^{+} -sites.²⁹ They can be assigned as follows: the peaks at 1810 cm^{-1} and 1797 cm^{-1} correspond to Cu^{+} -NO mononitrosyls, that evolve with increasing pressure to Cu^{+} -(NO)₂ di-nitrosyls characterized by doublet with ν_s and ν_{as} at 1825 cm^{-1} and 1730 cm^{-1} .^{29,30}

It is important to note, that the concentration of the Cu^{2+} and Cu^{+} species is lower than in the case of the ion exchange sample (K-Cu-LTL IE). Also, the species corresponding to the copper oxide are present, which is in a good agreement with the results from the CO adsorption study. It is worth mentioning the formation of two types of NO_x^- species that have not been observed on the other samples. According to the previous report,²⁹ the bands at 1660, 1565 and 1300 cm^{-1} previously observed in the CuY zeolite manifest the formation of the bridging nitrates and the bidentate nitrates; these are formed as a consequence of the NO_2 adsorption on isolated copper-oxygen species. It has been shown by Davydov et al.³² that the formation of the nitrates on the zeolite lattice and on the copper cations may lead to the distortion of the interaction between slightly-associated Cu^{2+} species. The Cu^{2+} become isolated and this can be observed by comparison of the spectra of ion exchanged (K-Cu-LTL IE) and in situ (H-Cu-LTL IS) samples under oxygen. On the contrary to the K-Cu-LTL IE sample, the intensity of the band at 1955 cm^{-1} decreased drastically, while the band at 1910 cm^{-1} increased with the formation of the surface nitrates on the H-Cu-LTL IS.

From the above observations, we can conclude the following: the as-synthesized K-Cu-LTL IS contains spectral features of the CuO in the spectra, confirming the existence of the occluded

extra-framework Cu. However, after ion exchange with ammonium chlorite the H-Cu-LTL IS sample reveal the Cu⁺-CO complexes characteristic for sample obtained via ion exchange (K-Cu-LTL IE). There are two possible explanations: part of Cu which interacts with CO and NO is in the extra-framework sites of the K-Cu-LTL IS sample and the other part is in the framework (1) or is not accessible to the probe molecules (2); the copper become accessible after interaction with NH₄Cl due to partial distortion of the crystal structure of the zeolite.

Hydroxyl Region in the IR spectra of copper containing zeolite samples

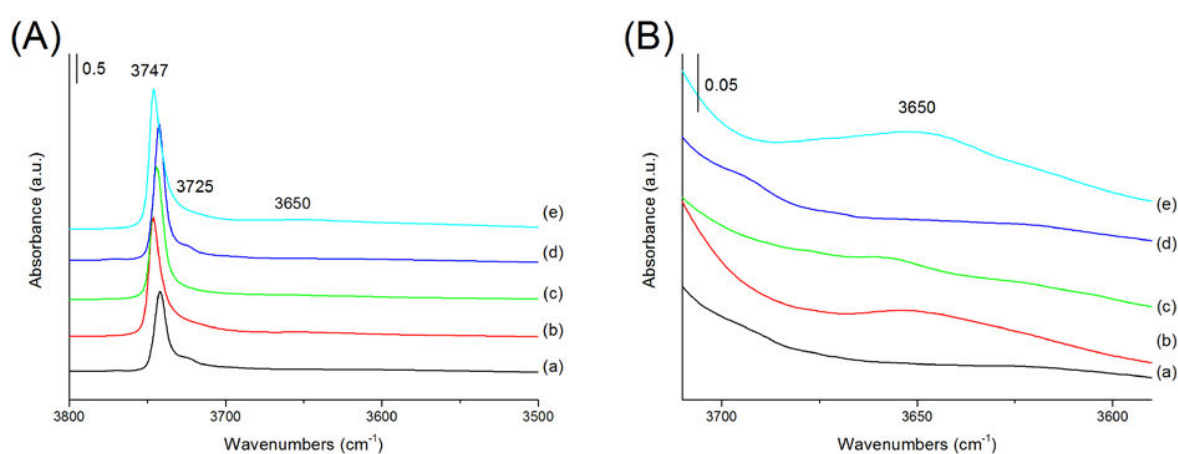


Figure 11 FTIR spectra for zeolite samples after evacuation at 673 K in the range of (A) 3800 – 3500 cm⁻¹ and (B) 3700 – 3600 cm⁻¹: (a) as-prepared parent K-LTL, (b) H-LTL, (c) K-Cu-LTL IE, (d) K-Cu-LTL IS and (e) H-Cu-LTL IS.

The hydroxyl region of the IR spectra was evaluated after thermal activation of samples in vacuum; under this treatment mainly water was removed from the zeolites.³³ The FTIR spectra of samples after pretreatment at 673 K for 14 h are shown in Figure 11. The bands at high frequencies result from the stretching vibrations of hydroxyl groups.¹⁶ The sharp maximum at ~3747 cm⁻¹ reflects the presence of the silanol hydroxyl groups located on the internal surface of the zeolite. Almost the same relative intensity of these bands is observed and this demonstrates the small size of the zeolite crystals. A weak band at 3725 cm⁻¹ in the spectra of parent K-LTL and H-LTL samples may be due to stretching vibrations of hydroxyl groups of internal silanol defects.^{16,33} No band at about 3670 cm⁻¹ is found that is generally assigned to

hydroxyl groups of Al(OH) described as extra framework aluminum species (EFAS) in all samples.³³ The weak band at 3650 cm^{-1} for samples H-LTL and H-Cu-LTL IS appears, which is a consequence of the ion exchange with NH_4Cl ; this is typical for stretching vibrations of unperturbed Brønsted acid sites (bridging $\equiv\text{Si}(\text{OH})\text{Al}\equiv$ hydroxyl groups).

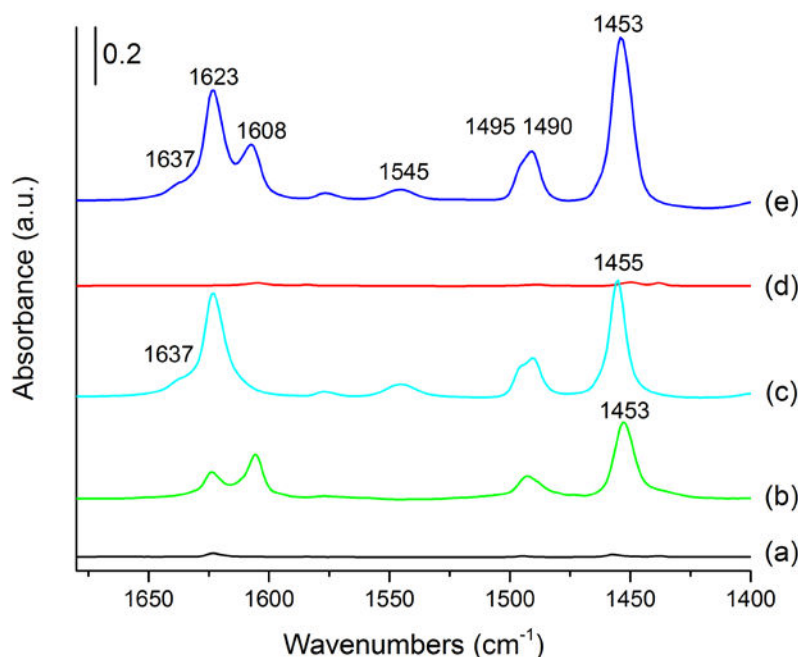


Figure 12 FTIR spectra of samples after pyridine adsorption at 423 K and evacuation at 523 K for 30 min: (a) as-prepared K-LTL, (b) K-Cu-LTL IE, (c) H-LTL, (d) K-Cu-LTL IS and (e) H-Cu-LTL IS

Pyridine Adsorption on copper containing zeolite samples

Pyridine (Py) adsorption on copper containing zeolite samples was carried out at 423 K followed by evacuation at 423-673 K with the step of 50 K for 30 min at each temperature. The FTIR spectra of the samples taken after evacuation at 523 K for 30 min are shown on Figure 12. The parent LTL, and K-Cu-LTL IS and K-Cu-LTL IE samples contain the Lewis acid sites (LAS). The pyridine is coordinated with extra-framework aluminum and copper cations, which is evidenced by the presence of bands at 1623 and 1455 cm^{-1} and 1608 and 1453 cm^{-1} , respectively.¹⁶ It is important to mention that the intensity of the latter bands increases after post-synthesis modification of the samples, probably due to partial destruction of the zeolite

structure. The LTL zeolite in proton form (H-LTL) and sample H-Cu-LTL IS contain Brønsted acid sites (BAS) as indicated by the presence of IR bands at 1545 and 1637 cm^{-1} . This confirms that the copper cations were exchanged by NH_4^+ ; the LAS are also measured, i.e. the bands at 1453-1455 cm^{-1} and 1623 and 1608 cm^{-1} are present. An important observation can be deduced from the spectrum of the copper-containing H-Cu-LTL IS sample. The intensity of the IR band at 1608 cm^{-1} is much higher than that for the K-Cu-LTL IS zeolite and is of the same intensity as for the K-Cu-LTL IE material, which shows the accessibility of extra-framework Cu^{2+} species after interaction with ammonium chlorate, thus confirming the above findings.

Conclusions

New copper-containing LTL type zeolite has been prepared by the facile organic template-free synthesis approach and systematically compared to the sample obtained via ion exchange method. It has been shown, that the state and behavior of copper in LTL zeolite strongly depend on the method used for the Cu inclusion. The direct incorporation of copper into the zeolite synthesis gel leads to the shrinkage of the unit cell parameters of the final crystals, while the post synthesis inclusion of copper leads to its expansion, which is probably caused by different affinity towards water of these two samples. The copper introduced by in situ synthesis approach shows distinct environment and occupies different position in comparison to the ion exchange sample. The copper is partially located in the zeolite framework and is unapproachable by the probe molecules (CO, NO and Pyridine). The post-synthesis modification of the sample with ammonium chlorate and high temperature treatment under oxygen cause the displacement of a significant amount of Cu to the extra-framework positions. This makes the copper species accessible for probe molecules. Some Brønsted acid sites are detected as well, that were not present in as-prepared materials, thus confirming the successful substitution of K^+ cations for NH_4^+ , while copper species remain intact.

References

- 1 K. G. Ione and L. A. Vostrikova, *Russ. Chem. Rev.*, 1987, **56**, 393–427.
- 2 K. G. Ione, L. A. Vostrikova and V. M. Mastikhin, *J. Mol. Catal.*, 1985, **31**, 355–370.
- 3 G. Perego, R. Millini and G. Bellussi, *Mol. Sieves*, 1998, **1**.
- 4 A. Sachse, V. Hulea, K. L. Kostov, E. Belamie and B. Alonso, *Catal. Sci. Technol.*, 2015, **5**, 415–427.
- 5 M. Milanova, R. Iordanova, K. L. Kostov and Y. Dimitriev, *J. Non. Cryst. Solids*, 2014, **401**, 175–180.
- 6 <http://europe.iza-structure.org/IZA-SC/framework.php?STC=LTL>
- 7 A. Kharchenko, O. I. Lebedev, V. Zholobenko, V. de Waele and S. Mintova, *J. Phys. Chem. C*, 2016, [acs.jpcc.6b08045](https://doi.org/10.1021/acs.jpcc.6b08045).
- 8 H. Van Bekkum, E. M. Flanigen, P. A. Jacobs and M. S. Rigutto, in *Studies in Surface Science and Catalysis*, 2001, pp. 911–955.
- 9 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 1967, **III**.
- 10 P. O. Fritz, J. H. Lunsford and C.-M. Fu, *Zeolites*, 1988, **8**, 205–208.
- 11 O. Larlus, S. Mintova and T. Bein, *Microporous Mesoporous Mater.*, 2006, **96**, 405–412.
- 12 R. R. Conry, *Encycl. Inorg. Chem.*, 2006, 1–19.
- 13 B. Murphy and B. Hathaway, *Coord. Chem. Rev.*, 2003, **243**, 237–262.
- 14 M. A. Cambor, S. B. Hong and M. E. Davis, *Chem. Commun.*, 1996, 425–426.
- 15 G. E. Bnown, G. V. Gibbs and P. H. Ribbe, *Am. Mineral.*, 1969, **54**, 1044–1061.
- 16 P. Kaminski, I. Sobczak, P. Decyk, M. Ziolek, W. J. Roth, B. Campo and M. Daturi, *J. Phys. Chem. C*, 2013, **117**, 2147–2159.
- 17 M. Rutkowska, U. Diaz, A. E. Palomares and L. Chmielarz, *Appl. Catal. B Environ.*, 2015, **168–169**, 531–539.
- 18 H. Praliaud, S. Mikhailenko, Z. Chajar and M. Primet, *Appl. Catal. B Environ.*, 1998, **16**, 359–374.
- 19 F. Giordanino, P. N. R. Vennestrøm, L. F. Lundegaard, F. N. Stappen, S. Mossin, P. Beato, S. Bordiga and C. Lamberti, *Dalt. Trans.*, 2013, **42**, 12741–61.
- 20 G. Centi and S. Perathoner, *Appl. Catal. A, Gen.*, 1995, **132**, 179–259.
- 21 H.-Y. Zheng, J.-Z. Wang, Z. Li, L.-F. Yan and J. Z. Wen, *Fuel Process. Technol.*, 2016, **152**, 367–374.
- 22 M. NARAYANA, S. CONTARINI and L. Kevan, 1985, **375**, 370–375.
- 23 S. Contarini and L. Kevan, 1986, 1630–1632.
- 24 Y. M. Zhukov, A. Y. Efimov, E. V Zhizhin, D. A. Pudikov and V. P. Petranovskii, 2016, **103**, 448–451.
- 25 <http://xpssimplified.com/elements/copper.php>
- 26 G. Turnes Palomino, C. Otero Areán, F. Geobaldo, G. Ricchiardi, S. Bordiga and A. Zecchina, *J. Chem. Soc. Faraday Trans.*, 1997, **93**, 189–191.

- 27 A. Zecchina, S. Bordiga, G. Turnes Palomino, D. Scarano, C. Lamberti and M. Salvalaggio, *J. Phys. Chem. B*, 1999, **103**, 3833–3844.
- 28 K. I. Hadjiivanov, *Adv. Catal.*, 2002, **47**, 307–511.
- 29 K. Hadjiivanov, *Catal. Rev.*, 2000, **42**, 71–144.
- 30 I. Sobczak, M. Ziolek, M. Renn, P. Decyk, I. Nowak, M. Daturi and J. C. Lavalley, *Microporous Mesoporous Mater.*, 2004, **74**, 23–36.
- 31 C. Lamberti, A. Zecchina, E. Groppo and S. Bordiga, *Chem. Soc. Rev.*, 2010, **39**, 4951–5001.
- 32 A. A. Davydov and Y. A. Lokhov, *React. Kinet. Catal. Lett.*, 1978, **8**, 47–52.
- 33 S. Bordiga, C. Lamberti, F. Bonino, A. Travert and F. Thibault-Starzyk, *Chem. Soc. Rev.*, 2015, **44**, 7262–7341.

Chapter 4

Copper containing LTL films for sensor application

Introduction

In the past decades, there is an increasing need in the selective sensors, that are able to detect gaseous pollutants such as CO, CO₂ and NO_x at low concentrations (ppm levels).¹

The versatility of the zeolites in terms of the pore structure, surface area, catalytic activity, particle dimensions, and morphology makes them attractive for sensor and membrane applications. Specifically, the high adsorption capacity, high surface area and porosity, presence of mobile ions, and catalytic activity are of interest for the selective chemical sensors preparation.²⁻⁵

Recent developments of synthesis procedures for zeolite nanocrystals and their arrangements in thin-to-thick films, membranes and hierarchical bodies have pushed them into new, diverse and economically significant applications that have not been recognized before. Zeolites can be grown or assembled as thin films on a variety of supports, both inorganic (e.g. glass, ceramic, metal) and organic (e.g. plastics, cellulose, wood). This allows to transfer some of the characteristic properties of zeolites (adsorption, catalysis, molecular recognition and diffusion) to a 2-dimensional structure and pushed their applications into a vastly expanded fields including low-dielectric constant (low-k) insulating materials for computer chips, membrane reactors, corrosion-resistant protective coatings for metallic alloys, and hydrophilic and antimicrobial coatings for gravity-independent water separation in space.⁶⁻⁸

Various techniques have been developed for deposition of zeolite crystals onto supports such as direct synthesis, seed methods and attachment of crystals on functionalized surfaces. Among these methods, a spin coating approach is widely applied due to its simplicity. Spin-on process

is fast and offers operating precision, flexibility, and high uniformity over different surfaces. Also, spin coating provides effective control on film thicknesses by varying the concentration of suspensions and the spin-on rotation rates.^{8,9}

It is also of great importance to evaluate the mechanical, interfacial and tribological properties of zeolite films as these are critically important in providing the necessary mechanical strength, fracture and wear resistance for the final integrated systems.⁷

Hence, this work focuses on the preparation and characterization of copper-containing LTL thin films assembled on silicon wafer, followed by measuring its capability for CO detection as single analyte. The copper-containing LTL films have been exposed to low concentrations of CO in the presence of water and characterized by *operando* IR spectroscopy.

Experimental

Materials

Cu-LTL zeolite was prepared according to the procedure described in Chapter 1.

Preparation of Cu-LTL thin films

Polyvinylpyrrolidone (PVP10, average molecular wt. 10000, Sigma-Aldrich), ethanol and water were used as solvents for the preparation of the films.

The zeolite films were prepared by spin-coating approach on silicon wafers using Wafer Spinner SPIN150-NPP. The silicon wafers with both polished sides were pre-cleaned with ethanol and acetone prior to film deposition. The Cu-LTL suspension with a concentration of solid particles (1 – 2 wt.%) was mixed with PVP10 (5 wt.% in ethanol or water) in the ratio of 1:10. This suspension was treated in the ultrasonic bath for 30 minutes and filtrated through syringe filters (450 nm) prior to spin deposition on the substrate. The rotation speed of 2000 min⁻¹ and duration of spinning for 30s were applied for the preparation of the films. This coating procedure was repeated until the desired film thickness was obtained. High temperature

treatment of the films at 450 °C for 3 h under argon atmosphere was applied to improve the mechanical properties of the films and to remove the binder (PVP).

Characterization

The short-range surface features and thickness of Cu-LTL films were examined by using a field-emission scanning electron microscope MIRA TESCAN at an accelerating voltage 30.0 kV.

Nanoindentation tests were conducted on a MTS NanoXP system using a Berkovich diamond indenter (minimal radius tip of 20 nm), in CSM (Continuous Stiffness Measurement) mode, allowing to measure of hardness and modulus all along the tip penetration. Load measurement sensitivity was 75 nN, displacement measurement sensitivity was 0.1 nm.

The detection of CO with copper containing zeolite films was followed by *operando* FTIR spectroscopy using the procedure described elsewhere^{3,10,11}. Prior to CO delivery, the films were subjected to activation in Argon atmosphere containing 5 % of hydrogen at 350 °C (heating rate of 2 °C/min) for 4 hours. All the experiments were performed at atmospheric pressure in argon flow containing 100 ppm of water by stepwise introduction of CO in the cell. The IR spectra were collected in a continuous mode (32 scans/spectrum) with a Tensor 27 spectrometer (Bruker) equipped with a DTGS detector.

Results and discussion

The suspensions of Cu-containing LTL crystals in water were spin-coated on square-shaped silicon wafers to form thin, quasi-continuous films. SEM top view images of the samples reveal that the nanosized crystals cover the entire surface of the substrate (Figure 1A). The size of the individual crystals is very difficult to estimate from the top and side views of the SEM pictures. However, the high density and the homogeneity of the films along the support can be clearly observed from the SEM pictures. The nanosized zeolite crystals are well packed and form dense

and homogeneous films with various thicknesses, which is achieved by several deposition steps (Figure 1B).

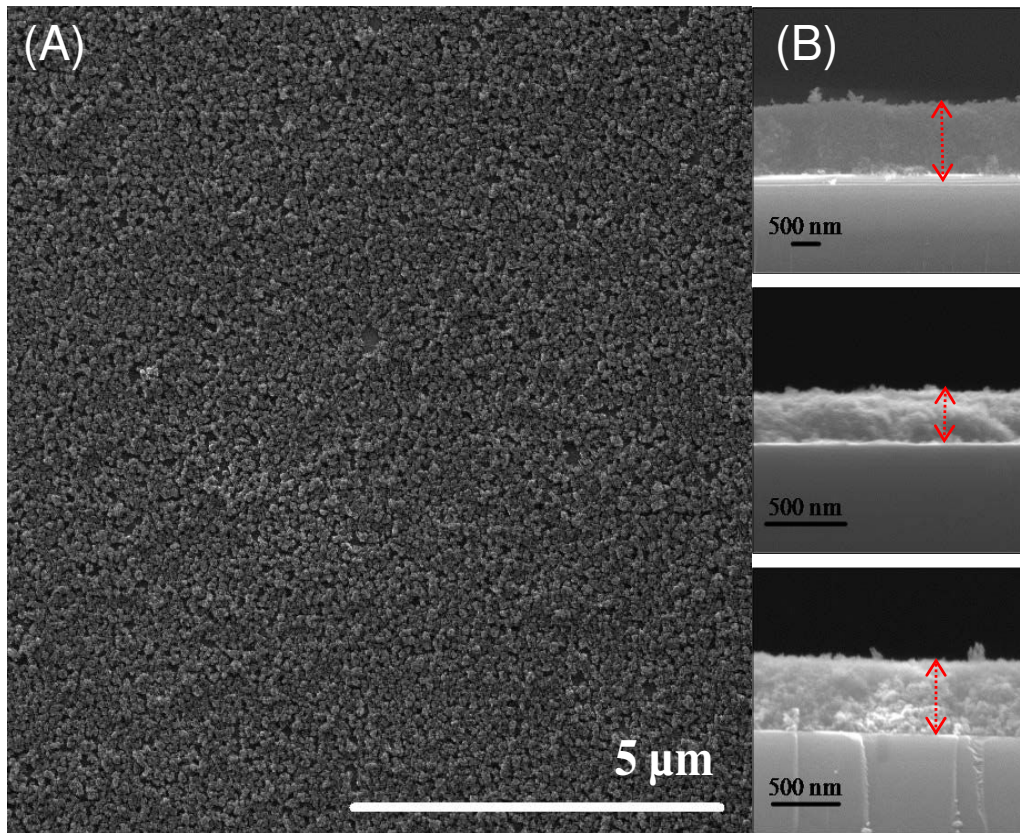
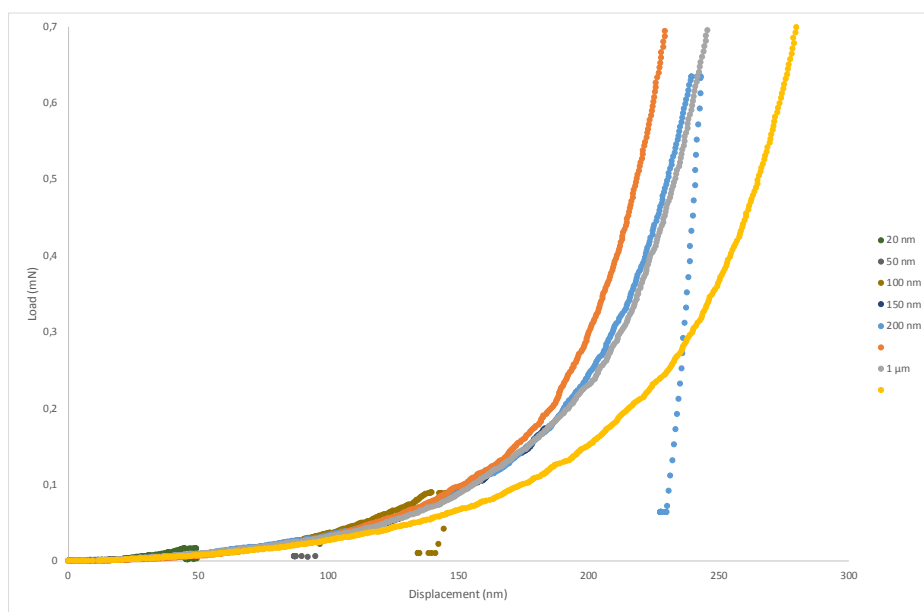


Figure 1 SEM pictures of Cu-LTL film after calcination: (A) top view and (B) cross-section images taken for Cu-LTL film with different thicknesses (from top to bottom the film thickness is 1200, 350 and 500 nm)

Nanoindentation test with a Berkovich diamond indenter was performed on the films with various thickness.⁷ The targeted depths were 20 nm, 50 nm, 100 nm, 150 nm, 200 nm, 500 nm, 1 μm, and 2 μm. However, the focus has been on measurements with a maximum depth of 200 nm (Figure 2).

(A)



(B)

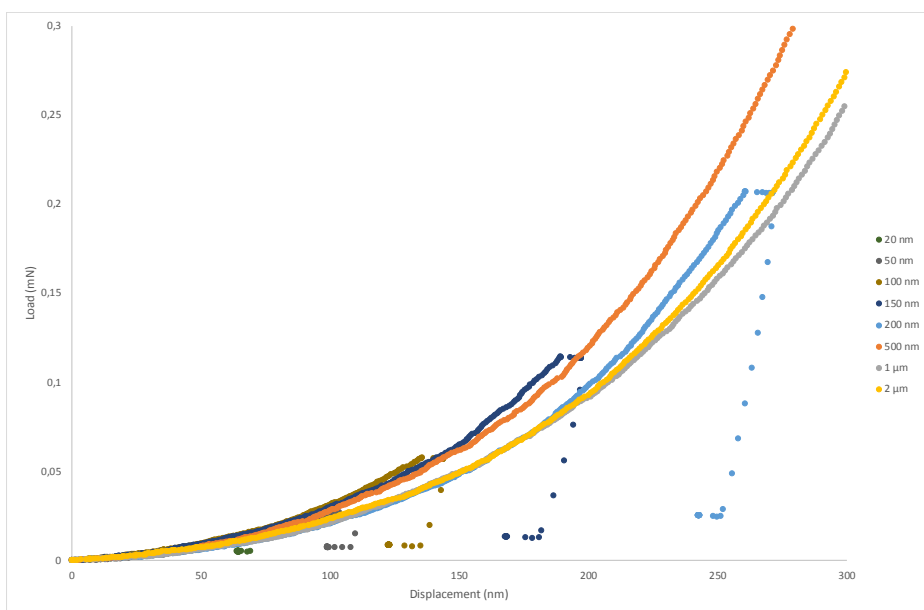


Figure 2 Loading curves for Cu-LTL films with a thickness of (A) 350 nm, (B) 500 nm (for 1200 nm is not shown). Good reproducibility of the measurements with a good superposition of the load-displacement curves for each measurement is obtained

The films show permanent deformation, the so called plastic behaviour which is linked to a residual deformation after unloading. This is confirmed by microscope observation of the indents after testing (see the light zone around the indents, reflecting the presence of the material plastic bulging, Figure 3). This probably reflects the unsticking of the film from the Si-wafer, caused by the deformation field induced by the indenter tip, as it penetrates the sample. This result may also be linked to a plastic behaviour of the film, but must strongly be correlated to the Si substrate visco-plastic deformation.

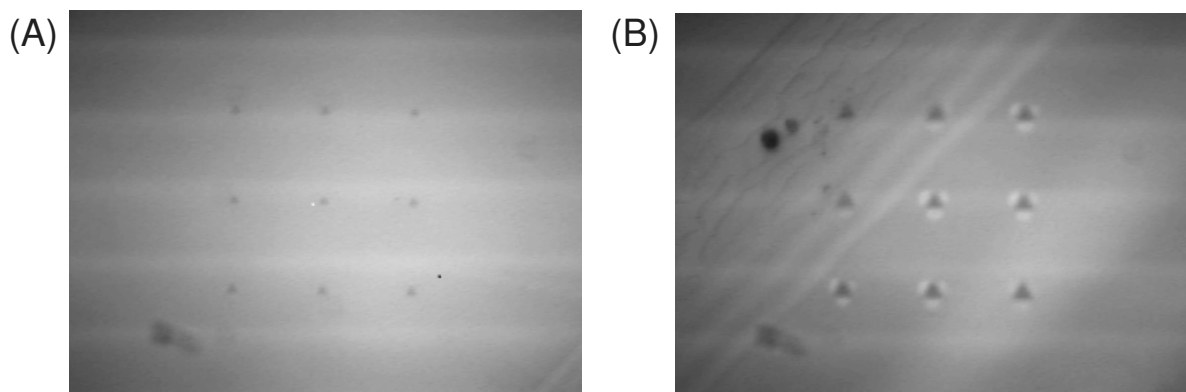
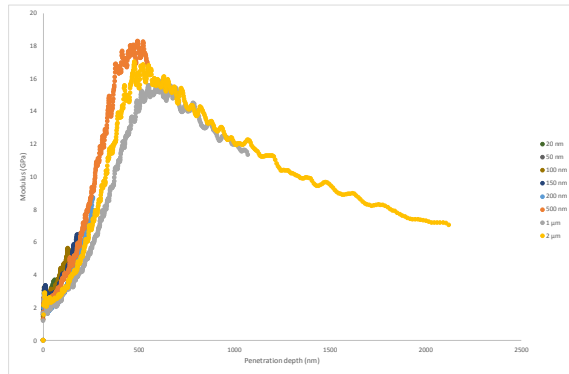


Figure 3 Micrographs of the indents for zeolite films with a thickness of 1200 nm with indentation depth of (A) 1 μm and (B) 2 μm

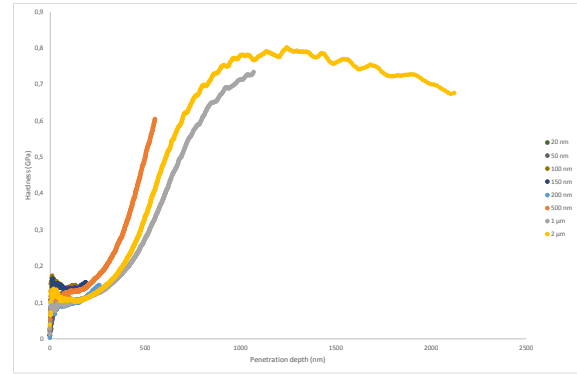
Evolution of modulus and hardness at different penetration depths has been measured using CSM mode, that allows obtaining data continuously during a nanoindentation process (Figure 4A, B). Principle is to superimpose small oscillation amplitude on the displacement (or load) signal and to measure the load (or displacement) response. These oscillations could be considered as series of loading-unloading processes done on very small depth intervals, so that the mechanical properties can be measured as a function of the indentation depth. This technique is particularly helpful for the characterization of coatings.

The influence of the substrate, that is much harder than the zeolite film (Young's modulus $E_{\text{Si wafer}} = 150\text{-}180 \text{ GPa}$ and hardness $H_{\text{Si wafer}} = 10\text{-}13 \text{ GPa}$ of the silicon wafer),^{12,13} is clearly visible with the significant increase of the mechanical parameters at a penetration depth up to 200 nm (Figure 4 C,D).

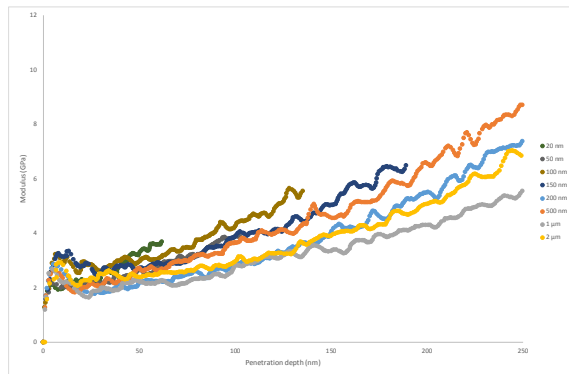
(A)



(B)



(C)



(D)

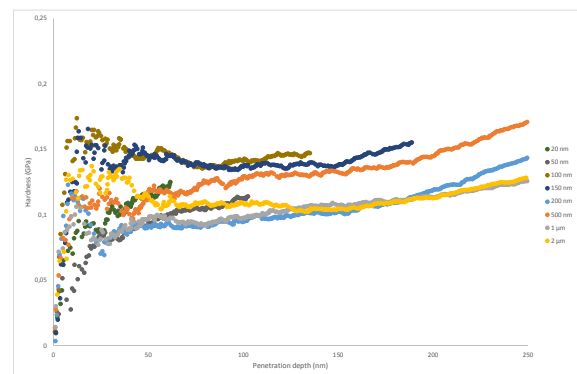


Figure 4 The evolution of modulus (A) and hardness (B) as a function of penetration depth from measurements done on Cu LTL sample with a thickness of 500 nm (middle thickness). The zoom on the measurements of modulus (C) and hardness (D) with the penetration depth less than 200 nm. The results obtained for the other two other samples with thicknesses of 350 and 1200 nm are similar and are not shown

The increase of modulus and hardness during the first stages of indenter penetration probably corresponds to surface phenomena due to mostly electrostatic interactions between sample and indenter tip.

Table 1 Modulus and hardness values of Cu-LTL films with thickness of 350, 500 and 1200 nm at indentation depth from 150 nm to 2000 nm

Cu-LTL film 350 nm				
Indentation depth (nm)	Modulus from loading (GPa)	Hardness from loading (GPa)	Modulus from unloading (GPa)	Hardness from unloading (GPa)
150	11.8 ± 5.4		25.32 ± 15.63	0.29 ± 0.09
200	12.39 ± 1.1	0.18 ± 0.02	37.85 ± 7.17	0.48 ± 0.09
500	17.92 ± 2.15	0.21 ± 0.02	58.91 ± 1.48	3.94 ± 0.12
1 000	12.51 ± 2.17	0.16 ± 0.02	43.09 ± 0.41	4.26 ± 0.13
Cu-LTL film 500 nm				
Indentation depth (nm)	Modulus from loading (GPa)	Hardness from loading (GPa)	Modulus from unloading (GPa)	Hardness from unloading (GPa)
150	4.39 ± 0.36	0.12 ± 0.01		
200	4.66 ± 0.53	0.12 ± 0.02	6.84 ± 0.73	0.16 ± 0.01
500	4.57 ± 0.32	0.12 ± 0.01	12.61 ± 0.26	0.59 ± 0.02
1 000	3.62 ± 0.34	0.11 ± 0.01	7.39 ± 2.78	0.79 ± 0.07
Cu-LTL film 1200 nm				
Indentation depth (nm)	Modulus from loading (GPa)	Hardness from loading (GPa)	Modulus from unloading (GPa)	Hardness from unloading (GPa)
150	3.27 ± 0.45	0.11 ± 0.01		
200	3.27 ± 0.26	0.11 ± 0.01	5.65 ± 0.26	0.12 ± 0.01
500	3.54 ± 0.20	0.11 ± 0.01	26.54 ± 0.77	0.50 ± 0.03
1 000	3.20 ± 0.30	0.10 ± 0.01	23.69 ± 0.44	1.71 ± 0.07

Values of the modulus and hardness obtained from unloading are preferable and allow to get more sensitive results correlated to the fact that during the first stage of unloading, only the elastic behaviour of the material is expressed (Table 1).

The rather good superposition of the loading curves and the low dispersion of the numerical results suggest a high homogeneity of the films. Increase of the hardness and modulus with the indentation maximum depth is due to the great influence of the substrate, as has been mentioned before. In order to eliminate the influence of the silica wafer on the results from the measurements, the focus has been put on the results obtained up to maximum penetration depth of 200 nm (Table 2).

Table 2 Modulus and hardness of Cu-LTL films with a thickness of 350, 500 and 1200 nm at indentation depth of 200 nm (upon loading)

<u>Cu-LTL film 350 nm</u>		
Indentation depth	Modulus	Hardness
(nm)	(GPa)	(GPa)
200	26.848	0.280
500	35.339	0.339
1 000	25.657	0.216
<u>Cu-LTL film 500 nm</u>		
Indentation depth	Modulus	Hardness
(nm)	(GPa)	(GPa)
200	5.496	0.118
500	6.543	0.145
1 000	4.303	0.113
<u>Cu-LTL film 1200 nm</u>		
Indentation depth	Modulus	Hardness
(nm)	(GPa)	(GPa)
200	4.196	0.116
500	4.943	0.128
1 000	4.206	0.104

Table 3 Modulus and hardness of Cu-LTL films with a thickness of 350, 500 and 1200 nm at indentation depth of 50 nm (upon loading)

	Modulus (GPa)	Hardness (GPa)
Cu LTL 350	6.273 ± 0.916	0.124 ± 0.136
Cu LTL 500	3.893 ± 0.465	0.119 ± 0.018
Cu LTL 1200	2.597 ± 0.563	0.121 ± 0.018

According to the results for the samples with the thickness of 500 nm and 1200 nm, the modulus and hardness of the films seems to be not much sensitive to the films thickness ($E_f = 2.5\text{-}4.5$ GPa and $H_f = 0.1\text{-}0.2$ GPa).

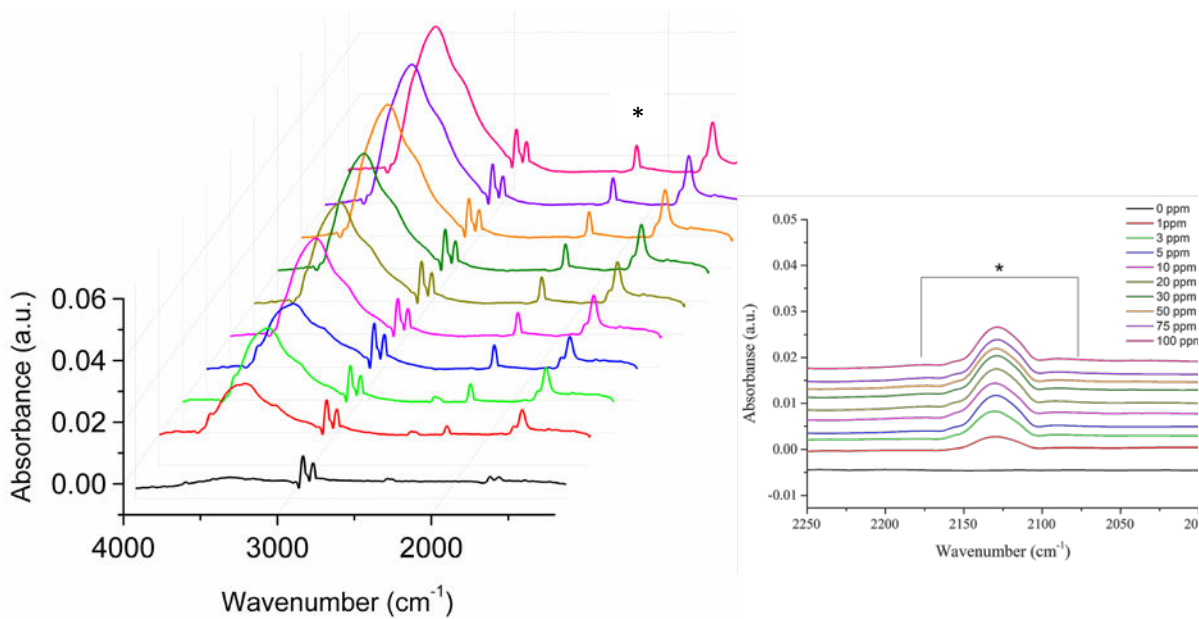
The higher values of the mechanical parameters measured for the film with a thickness of 350 nm is due to the influence of the Si-wafers. The measurements performed at very small penetration depth (20 nm and 50 nm) have been set to avoid this matter; however, both the surface interaction between the sample and the tip, and the roughness of the film even very small is significant at this penetration depths. This leads to a huge dispersion in modulus and hardness numerical values, thus not reliable mechanical parameters for such film thickness ($t = 350$ nm) are obtained.

Compared to values found in the literature¹² for the modulus and the hardness for zeolites deposited on silicon wafers, produced for semiconductor electronic applications, the values obtained in this study are a bit lower, but of the same order of magnitude ($E = 10\text{-}18$ GPa, $H = 0.3\text{-}1.2$ GPa). Such difference might be due to either a variation in the chemical composition or a higher porosity of the films.

Detection of carbon monoxide

The Cu-LTL zeolite films were used for detection of low concentration of carbon monoxide as a single analyte. The detection of CO was performed with Cu loaded zeolite film with a thickness of 500 nm and followed by operando IR spectroscopy. The results were further compared with the CO detection with parent LTL thin films of the same thickness. Prior to the measurements, the films were activated at 350 °C under argon atmosphere with 5% hydrogen, and then different CO concentrations (1–100 ppm) were delivered to the reaction cell with the film. The evolution of IR spectra of CO adsorbed on parent LTL and Cu-LTL films is shown on Figure 5. The IR spectra for Cu-LTL film at 25 °C represents a band around 2128 cm^{-1} characteristic of CO adsorbed on Cu^+ species, that have been previously described in the Chapter 3.¹⁴ As can be seen from Figure 5, 1 ppm of CO is the lowest concentration detected by the Cu-LTL film, whereas pure LTL is not sensitive to CO. The increase of the CO concentration measured at 25 °C resulted in a Langmuir type evolution of the CO peak centered at 2128 cm^{-1} . The saturation of Cu-species is reached at higher concentration of CO, that is expressed by a plateau on the graph (Figure 6), while for parent LTL the CO adsorption is negligible at room temperature and could be attributed to its physisorption.

(A)



(B)

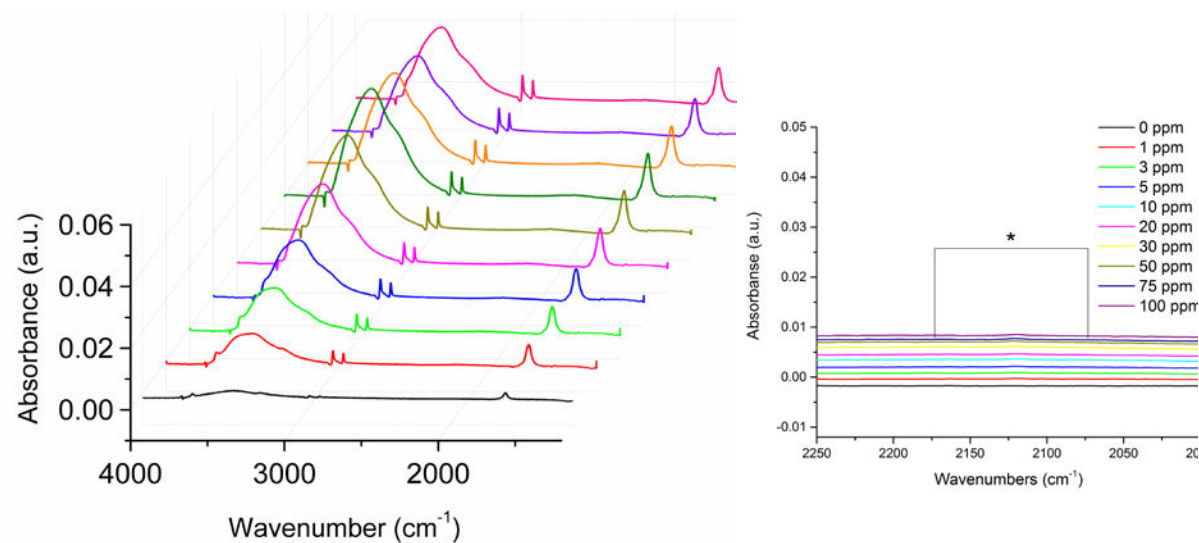


Figure 5 The evolution of IR spectra of CO (1 to 100 ppm) detected by (a) Cu-LTL and (b) parent LTL films with the thickness of 500 nm; the peak at 2128 cm⁻¹ is marked with an asterisk *

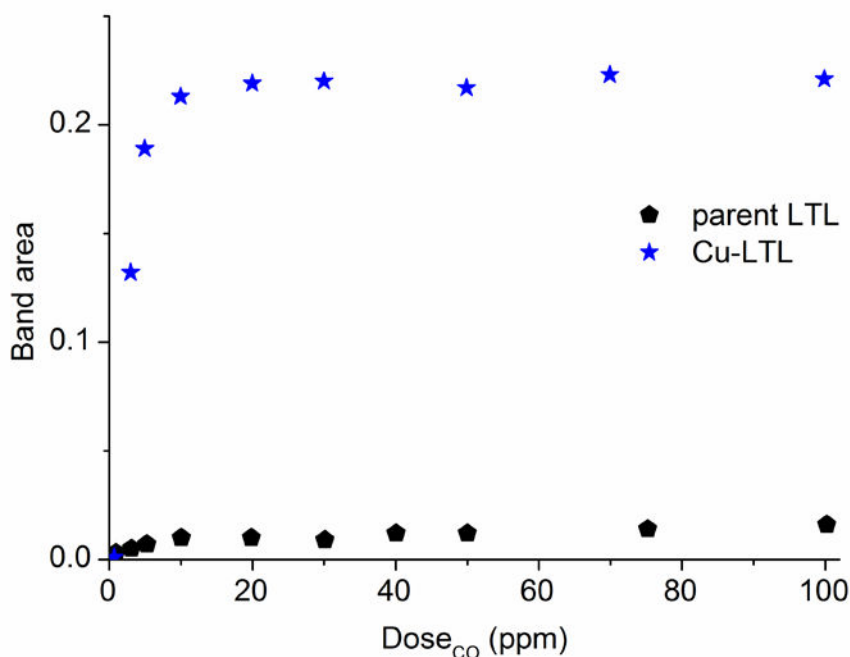


Figure 6 Evolution of the CO band area of the peak at 2128 cm^{-1} in the IR spectra of parent LTL and Cu-LTL films measured at $25\text{ }^{\circ}\text{C}$

Conclusions

Copper containing LTL zeolite films (Cu-LTL) were deposited on silicon wafers and thoroughly characterised by SEM and nanoindentation. The thickness of the Cu-LTL films can be controlled by tailoring the concentration of the coating zeolite suspensions, number of deposited layers and spinning speed during spin coating procedure. The modulus and hardness of the Cu-LTL films were measured as a function of the indenter penetration depth for maximum-targeted depth ranging from 20 nm to 2000 nm. Three samples with the same film composition but with different thicknesses (350, 500 and 1200 nm) were investigated. The thickness, modulus and hardness show the independence for the film thickness ($E_f = 2.5\text{-}4.5\text{ GPa}$ and $H_f = 0.1\text{-}0.2\text{ GPa}$).

The Cu-LTL films were further employed for detection of low concentration of CO at ambient conditions. Compared to the pure LTL, the Cu-LTL zeolite films exhibit high sensitivity and fast response towards low concentrations of CO (1-100 ppm). The response of the Cu-LTL films towards CO at 1 ppm has been measured; the results clearly point out that the Cu-LTL

films are good candidates for sensing application due to their remarkable mechanical and thermal stability mainly determined by the method of preparation.

References

- 1 S. N. Talapaneni, J. Grand, S. Thomas, H. A. Ahmad and S. Mintova, *Mater. Des.*, 2016, **99**, 574–580.
- 2 S. M. Auerbach, K. A. Carrado and P. K. Dutta, *Handbook of zeolite science and technology*, CRC Press, 2004, vol. 2004.
- 3 S. Thomas, P. Bazin, L. Lakiss, V. De Waele and S. Mintova, *Langmuir*, 2011, **27**, 14689–14695.
- 4 H. Xiao, J. Zhang, J. Dong, M. Luo, R. Lee and V. Romero, *Opt. Lett.*, 2005, **30**, 1270–2.
- 5 J. Zhang, M. Luo, H. Xiao and J. Dong, *Chem. Mater.*, 2006, **18**, 4–6.
- 6 M. P. Pina, R. Mallada, M. Arruebo, M. Urbiztondo, N. Navascués, O. De La Iglesia and J. Santamaria, *Microporous Mesoporous Mater.*, 2011, **144**, 19–27.
- 7 M. C. Johnson, C. M. Lew, Y. Yan and J. Wang, *Scr. Mater.*, 2008, **58**, 41–44.
- 8 T. Babeva, H. Awala, M. Vasileva, J. El Fallah, K. Lazarova, S. Thomas and S. Mintova, 2013, 3009–3014.
- 9 J. Kobler, H. Abrevaya, S. Mintova and T. Bein, *J. Phys. Chem. C*, 2008, **112**, 14274–14280.
- 10 T. Babeva, H. Awala, M. Vasileva, J. El Fallah, K. Lazarova, S. Thomas and S. Mintova, *Dalton Trans.*, 2014, **43**, 8868–8876.
- 11 X. Zou, J.-M. Goupil, S. Thomas, F. Zhang, G. Zhu, V. Valtchev and S. Mintova, *J. Phys. Chem. C*, 2012, **116**, 16593–16600.
- 12 M. Johnson, Z. Li, J. Wang and Y. Yan, *Thin Solid Films*, 2007, **515**, 3164–3170.
- 13 H. Sjöström, I. Ivanov, M. Johansson, L. Hultman, J. E. Sundgren, S. V. Hainsworth, T. F. Page and L. R. Wallenberg, *Thin Solid Films*, 1994, **246**, 103–109.
- 14 K. I. Hadjiivanov, *Adv. Catal.*, 2002, **47**, 307–511.

Chapter 5

The plasmonic chemistry of silver containing nanosized zeolite film revealed by transient absorption spectroscopy

Introduction

When an optical radiation excites a metal nanoparticle (NP) in resonance with the plasmon band, the energy of the incident photons is absorbed by the free electrons (conduction electrons), which in response populate the levels of energy located above the Fermi level of the metal. These excited electrons are named “hot-electrons” because in this non-equilibrium state, the electronic temperature (T_e) is higher than the temperature of the metal lattice (T_{ph}). The main dissipation channel of the excess of energy injected in the hot-electrons is the thermalization with the lattice by electron-phonon coupling. This mechanism induces an increase of the temperature of the metal, and this is notably the origin of the photothermal applications of the NP. Besides, the hot-electrons can also directly interact with molecules (or solids) that are located near the surface of the NP, resulting in their excitation and possibly their chemical activation. This particular reactivity of the hot-electrons, associated with the recent advances in the preparation and characterization of nanosized materials have triggered a widespread interest for researches in plasmonic chemistry.¹⁻⁴ The main target is to exploit the hot-electron-driven-chemistry for solar-to-chemical energy conversion applications. The large-scale exploitation of this novel technology is conditioned by the discovery of efficient materials. Conceptually, the performance of these materials depends on the optical and electronic properties of the metal NPs, but the metal-support interactions have also been identified as a critical parameter.⁵

Microporous materials and more specifically zeolites are recognized as appropriate supports for metal NPs. For example, gold NPs supported on the external surface of zeolite crystals were

considered for plasmonic chemistry applications through an investigation of the photocatalytic oxidation of aromatic alcohols.^{6,7} The benefits of using zeolites as support for metal NPs for plasmonic chemistry are related to the ability (i) to disperse and stabilize very small metal NPs, without the need of a capping agents, so that the surface of the NPs remains accessible to the reactants, and (ii) to concentrate the reactants by adsorption on the zeolite surface, thus favoring their interactions with the supported NPs. However, one major drawback of zeolite crystals for light-driven applications is that most of them are prepared with a size in the range of several micrometers that strongly scatter the visible light, and thus they are difficult to be implemented into optical devices.

In the last decades, a lot of effort have been paid on the development of syntheses approaches toward preparation of nanosized zeolites,^{8,9} i.e., zeolite crystallites with a size in the range 5-100 nm. Recent papers reported on the preparation of the most industrially useful zeolites with FAU, EMT, BEA, MFI, LTL- framework type structures with nanosized dimensions.¹⁰⁻¹⁴ The nanosized zeolites possess characteristics similar to those of their bulky counterpart with, in addition, a much higher external surface to bulk volume ratio. Besides the nanosized zeolites can be easily assembled in the form of thin-to-thick films or three-dimensional bodies with very good transport and optical properties.^{13,15,16} The nanosized zeolites are also hosts for stabilization of metal or semiconductor nanoparticles,^{17,18} Pt,¹⁹ Pd,²⁰ Ag^{21,22} or Cu.²³ So far metal-containing nanosized zeolites assembled in films have still never been considered as a material for plasmonic chemistry.

This work deals with LTL nanosized zeolites used as a host for nm-sized silver NPs, and explores the potential of this material for hot-electrons driven chemistry applications. This issue is addressed by using UV-vis transient absorption spectroscopy, which proved to be a method of choice to characterize the hot-electrons dynamics,²⁴⁻²⁷ and their coupling with the surrounding media.^{26,28} Up to now, ultrafast pump-probe measurements in zeolites remain quite

seldom.^{29–33} These measurements are performed essentially either on micron-sized crystalline powders or on colloidal suspensions consisting of nanosized zeolites.^{21,34,35} The latter approach allows to perform transient absorption measurements in transmission, but it would be of limited interest in the context of plasmonic chemistry due to the lack of control of the metal surrounding in the solution. In order to address the ultrafast processes involved in the plasmonic behavior of metal-zeolite host-guest systems, we explore a novel route consisting of transient absorption measurements on transparent films consisting of nanosized zeolites. This approach notably offers the possibility of controlling the micro-environment of the metal nanoparticles in the zeolite host-guest systems. In the current study, we investigated the plasmonic response of silver nanoparticles (Ag NPs) in LTL-type zeolite films under vacuum atmosphere. The preparation of Ag NPs in the nanosized LTL- type zeolites, followed by the preparation of the transparent films, and testing of their compatibility with the requirements of the transient absorption spectroscopy are presented. The ultrafast plasmonic response of these materials is reported too.

Experimental

Synthesis and characterization of silver-containing LTL zeolite crystals

Aluminum hydroxide (reagent grade, Sigma-Aldrich), ludox SM colloidal silica (30 wt. % suspension in H₂O, Sigma-Aldrich), and potassium hydroxide (ACS reagent, > 85 %, pellets, Sigma-Aldrich). The initial precursor solution with a chemical composition: 5 K₂O : 10 SiO₂ : 0.5 Al₂O₃ : 200 H₂O was prepared *via* dissolving 40.0 mmol Al(OH)₃ (3.9 g, 80 wt.% Al(OH)₃; 20 wt.% H₂O; A2100) and 0.4 mol potassium hydroxide (23.3 g, KOH, Aldrich) in 86.0 g double distilled water (dd H₂O) and 0.4 mol SiO₂ (83.1 g, Ludox SM30, Aldrich). This mixture was stored for one day on an orbital shaker, and additionally stirred for one more day to obtain a water-clear precursor suspension. Further the synthesis was performed at 170 C for 18h.

The nanosized LTL zeolite crystals with rectangular shape (20-40 nm) were recovered by multistep centrifugation (20000 rpm, 40 min) and dispersed in doubly distilled water until the pH of the decanted solution reached 8. Prior to incorporation of silver cations, the LTL nanocrystals were stabilized in water at pH=7.5-8 with a concentration of solid particles of 7.5 wt %.

Silver nitrate (>99.9%, Alfa Aesar) or silver perchlorate (>99.9%, Alfa Aesar) were used for the ion exchange treatment of the LTL zeolite. The ion-exchange was carried out directly in the colloidal suspension without preliminary drying of the sample, as follows: 20 mL silver perchlorate solution with a concentration of 0.05 M was added to the LTL zeolite suspension (7.5 wt %, 12 mL) and the mixture kept for 4 h at room temperature. The ion-exchanged samples were purified three times via high-speed centrifugation and re-dispersed in water. The silver nanoparticles (Ag NPs) in the LTL zeolite suspensions (2 wt.%, 7 mL) were prepared under microwave irradiation (120 ° C, 10 min, 1000 W) in the presence of a triethylamine (>99 %, Sigma-Aldrich) as a reducing agent (C_2H_5N , 2 mL). The reduced suspension was again purified three times and dispersed in water.

The crystalline structure of the nanosized zeolite crystals before and after ion exchange with silver was determined by recording the powder X-ray diffraction (XRD) patterns using a PANalytical X'Pert Pro diffractometer with Cu Ka monochromatized radiation (1:5418 Å). The samples were scanned in the range 4 to 80 °2 θ , with a step size of 0.02 °2 θ . The size and location of the Ag NPs were further studied by high angle annular dark field (HAADF) and annular bright field (ABF) scanning transmission electron microscope (STEM). These studies were performed using a JEOL ARM200F cold FEG double aberration corrected electron microscope operated at 200 kV equipped with a large solid-angle centurio EDX detector and Quantum EELS spectrometer.

The UV–vis absorption spectra of the zeolite films containing Ag NPs were recorded on a Varian Cary 4000 Spectrophotometer working in transmission mode.

Preparation and characterization of silver-containing LTL zeolite films

The CaF_2 optical plates (1 mm thick) were used as film supports for all spectroscopic measurements; the plates pre-cleaned with ethanol and acetone prior to film deposition.

Polyvinylpyrrolidone (PVP10, average mol. wt. 10,000, Sigma-Aldrich), Poly(diallyldimethylammonium chloride) (PDADMAC, 20 wt. % in H_2O) were used without further purification as binders in order to prepare films with good mechanical properties. Ethanol (Sigma-Aldrich, 98 %) and doubly distilled water were used as solvents.

The zeolite films were prepared by spin-coating approach on CaF_2 optical plates (1 mm thick, 13 or 20 mm in diameter) using Wafer Spinner SPIN150-NPP. The surface of the plates was modified by chemical anchoring of seed crystals (parent LTL) on Poly(diallyldimethylammonium chloride) adsorbed on the surface of substrate. The pre-cleaned plates were immersed in 5 wt.% solution of polymer for 20 minutes, thoroughly rinsed with distilled water and dipped in the LTL solution for another 20 minutes. This procedure was repeated three times, and the seed layer obtained (thickness of 50 nm) was calcined at 450°C for 3 h at a heating ramp of 3°C min^{-1} .

The Ag-LTL suspension with a concentration of solid particles (2 wt.%) was mixed with PVP10 (5 wt.% in ethanol or water) in the ratio of 1:10. This suspension was treated in the ultrasonic bath for 30 minutes and filtrated through syringe filters (450 nm) prior to spin deposition on the seeded CaF_2 plates. The rotation speed of 5000mn^{-1} and duration of spinning for 30 s were applied for the preparation of the films. This coating procedure was repeated until the desired film thickness was obtained. High temperature treatment of the films at 450°C for 3 h under argon atmosphere was applied to improve the mechanical properties of the films and to remove the binder.

The as-prepared films, hereafter named AgLTL, was further calcined under the same conditions (450°C for 3 h) prior time-resolved measurements.

FTIR measurements of silver-containing LTL zeolite films

The spatial thickness variation of the AgLTL films over the support was characterized by FTIR imaging. The spectra were obtained in transmission mode using a FTIR imaging system consisting of a Bruker Hyperion 3000 microscope coupled with a FTIR spectrometer using a x36-Cassegrain objective. The infrared images were recorded with a Focal Plane Array (FPA 64x64 pixels) detector covering a spatial area of $71 \times 71 \mu\text{m}^2$ ($1.1 \times 1.1 \mu\text{m}^2$ per pixel). Single point ($60 \times 60 \mu\text{m}^2$) IR spectra were acquired with a MCT detector. Typically, the spectra were reconstructed from a total of 256 interferograms with a spectral resolution of 4cm^{-1} .

Femtosecond transient absorption measurements of silver-containing LTL zeolite films

Figure 1 shows an overall scheme of the UV-vis transient absorption setup and vacuum sample cell used to perform the femtosecond pump-probe measurements on nanozeolite thin films.

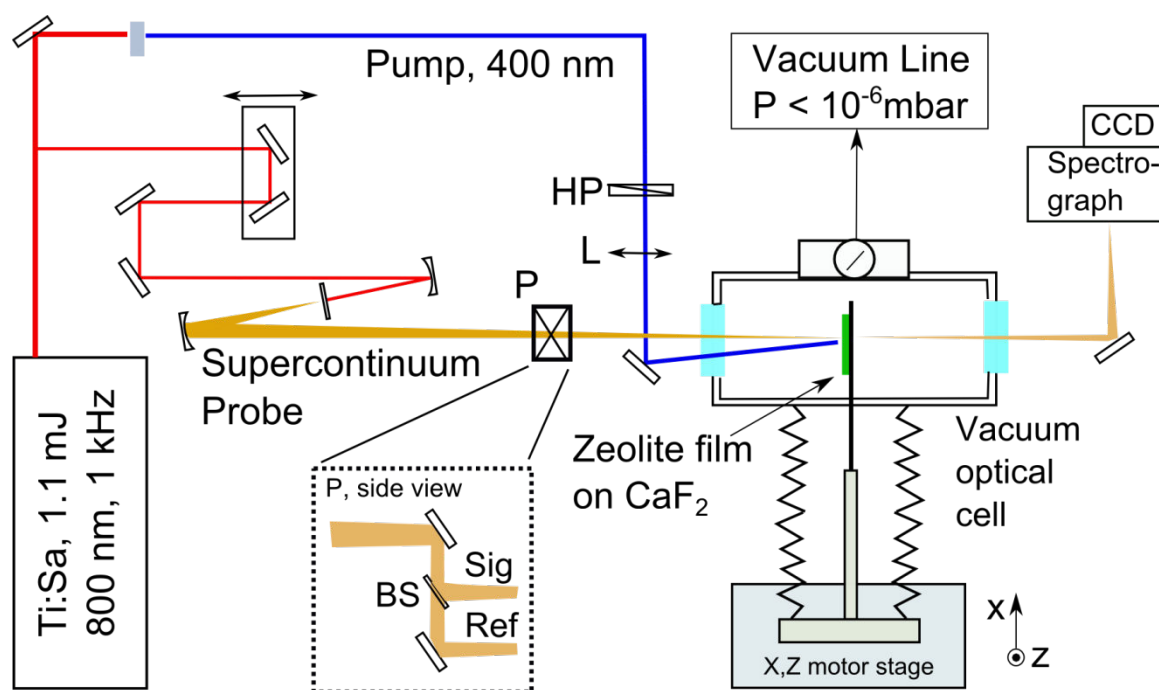


Figure 1 Transient absorption setup: a sample plate is mounted on a motorized XZ translation stage and placed inside a homemade optical vacuum cell. The 400 nm pump excitation beam is focused (lens L) slightly ahead of the sample. The super-continuum is split into signal (Sig) and reference (Ref) beams using a periscope (P) composed of a broadband beam-splitter (BS). Both Sig and Ref beams are passing through the sample and detected by a CCD camera

Broadband UV-vis transient absorption set-up

The pump and probe pulses are generated using an amplified 1kHz Ti:Sa laser system (Libra, Coherent) that delivers 90 fs (1.1 mJ) laser pulses at 800 nm. The pump excitation at 400 nm is generated by frequency-doubling the 800 nm fundamental in a BBO crystals (1 mm thick). As a probe beam, a white light super-continuum is generated by focusing a part of the fundamental beam (800 nm) in a 1 mm thick CaF₂ rotating plate. The pump is polarized parallel to the probe. The time delay between the pump and probe pulses is controlled by an optical delay line (Microcontrol Model MT160-250PP driven by an ITL09 controller) placed in front of the supercontinuum generation stage. The transient absorption spectra are recorded according to an acquisition set-up already described elsewhere.³⁶ Briefly, the 400 nm pump excitation beam is focused before the sample so that the diameter of the excited area is slightly larger than 0.5 mm (diameter). White light supercontinuum is split into a probe beam overlapping the pump beam in the sample, and a reference beam parallel to it and passing through the sample out of the pump beam is applied. The transmitted probe and reference lights are dispersed with a spectrograph and detected on two different channels of a CCD optical multichannel analyzer (Princeton Instrument LN/CCD-1340/400-EB detector with ST-138 controller). The acquisition is controlled by a pair of synchronized optical choppers that modulate the pump (25 Hz) and the probe (50 Hz) beams. The CCD camera is read at 50 Hz.

Optical cell

A stainless steel optical vacuum cell has been purposely designed, and assembled for the present spectroscopic investigation of nanosized zeolite films. It consists of an octagonal vacuum chamber (Kimball Physics) equipped with 2-mm thick CaF₂ windows mounted on CF flanges (MDC vacuum). The CaF₂ plate coated with the zeolite film is mounted on a motorized translation stage (Owis) allowing its continuous displacement in the plane XZ perpendicular to the light propagation. It is coupled to the optical cell via a flexible stainless steel bellow. The

ensemble is connected to a vacuum line equipped with a turbo-molecular pump. The set-up can be evacuated below 10^{-6} mbar.

Results and discussion

Preparation of LTL zeolite crystals containing silver nanoparticles

Silver was first introduced in the nanosized LTL zeolite crystals by ion-exchange method. The highly crystalline LTL-type structure of the zeolite samples before and after ion-exchanged was confirmed by XRD measurements. The silver-containing colloidal zeolite suspension, initially white, after chemical reduction became a green-yellow, which is the first indication that the silver cations were reduced, and silver nanoparticles were formed. The as-prepared silver containing LTL suspension (AgLTL) is stable for 24 months at room temperature. The formation of Ag NPs was firstly confirmed by transmission electron microscopy. Figure 2 shows an HAADF-STEM image of nanosized zeolite crystals taken after the reduction of Ag^+ to Ag^0 in the LTL suspension (see experimental part for more details). The LTL nanosized crystals with well-defined rectangular shape, sharp edges and a size of individual grain of 20-40 nm are shown in Figure 2. The crystalline fringes associated with the LTL lattice appear clearly, thus confirming the preservation of the crystal structure during the post-synthesis (ion exchange) treatment. Homogeneously dispersed Ag NPs appearing as white spots located mostly on the external surface of the LTL nanocrystals are seen in HAADF-STEM images. The enlarged picture shows also small Ag NPs align along the LTL channels suggesting that they fit inside the LTL nanocrystals. The size distribution of Ag NPs determined from the HAADF-STEM images (Figure 2), is narrow with a maximum at 1.3 nm and with ~80 % of the NPs having a diameter between 1.1 and 2.65 nm (500 particles measured). In Figure 2 a curve giving the number of silver atoms per NP versus the NP diameter is also represented, assuming an icosahedral NPs geometry. According to this model, silver NPs with a diameter in the range 1.1-2.65 nm are constituted by 55 to 930 atoms.

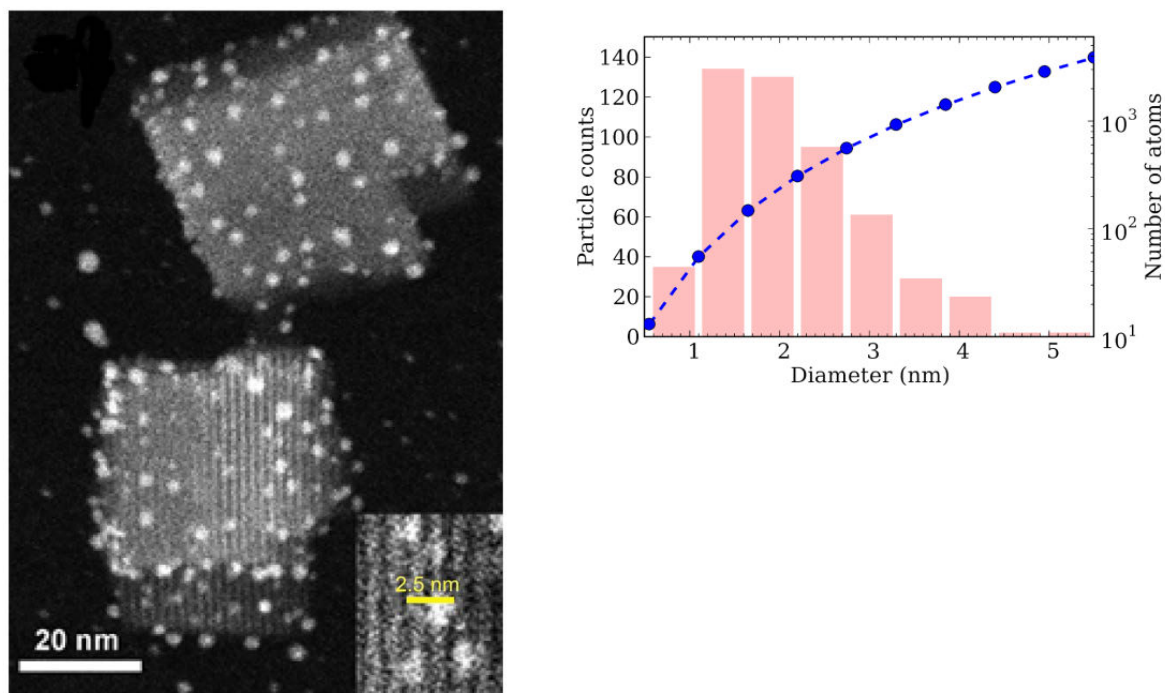


Figure 2 (left) HAADF STEM image of nanosized LTL zeolite crystals containing silver nanoparticles. (right) Histogram of the particles size distribution determined from a set of HAADF-STEM images (pink bars), and plot of the number of silver atoms per nanoparticle, calculated assuming an icosahedral NP shape, as a function of the NP size (blue trace)

Preparation and characterization of transparent silver-containing LTL zeolite films on CaF_2

Transient absorption measurements in thin zeolite layers have not been reported up to now. It is, thus, particularly important to carefully control the optical characteristics of such films and their resistance to light irradiation. Above all, the films must be transparent and weakly light diffusing. Another important parameter for long-term development of pump-probe measurements is a high spatial homogeneity of the films. To limit photodegradation during pump-probe measurements, it is necessary to move the sample back and forth for continuously refreshing the irradiated volume.

The zeolite nanocrystals from the AgLTL suspension were assembled in dense and homogeneous films on 1 mm thick CaF_2 plates. As can be seen in Figure 3-a, the as prepared films, named AgLTL, present a good transparency over the UV-Vis spectral range, a weak scattering background, and a maximum absorbance of the silver NPs of 0.3 (450 nm). The UV-

Vis absorption spectrum recorded in transmission mode exhibits the expected spectral signature of nm-size silver NPs: (i) the onset of the interband transition around 320 nm, and (ii) the plasmon band with a broad maximum at 420-430 nm with a width slightly below 100 nm.

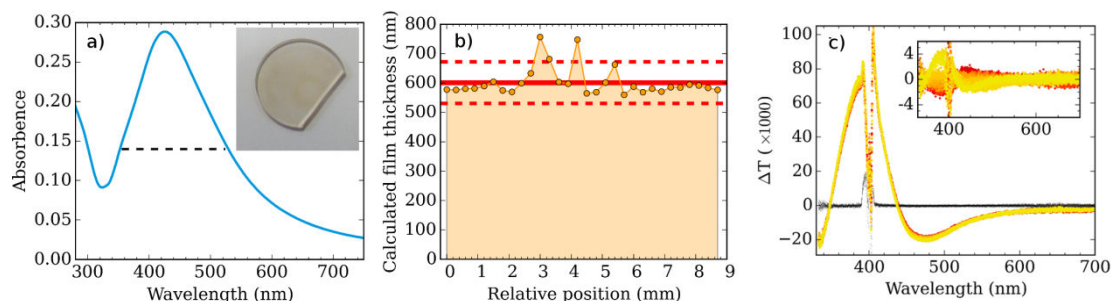


Figure 3 Characterization of AgLTL films: a) UV-vis absorption spectrum; inset: picture of the AgLTL zeolite film deposited on CaF_2 support. b) Thickness measurements deduced from the FTIR absorption in the spectral range $1300\text{--}900\text{ cm}^{-1}$ recorded at different positions along a 9 mm line at the center of the sample. The red traces give the average value of the thickness (full line) and the incertitude (dash-line). c) Series of transient absorption spectra of AgLTL excited at 400 nm and recorded alternatively for the pump-probe delay -1 ps and +1 ps. The inset shows the difference of each spectrum with the average of all the spectra, for the delay +1 ps

The spatial homogeneity and the thickness of AgLTL were quantified by using the FTIR spectroimaging technique, which is a fast and reliable method for characterizing materials in a quantitative and non-destructive way. Zeolites possess specific vibrational signatures in the Mid-IR spectral range. Here, the variation of the film thickness was obtained by monitoring the intensity of the infrared absorption associated with the (T = Si, Al) elongation modes of the zeolite framework as a function of the probed position on the film surface. After a calibration of the intensity of the IR bands at $1300\text{--}900\text{ cm}^{-1}$, the thickness of the AgLTL was quantitatively deduced (see SI). Figure 3-b shows the values of the thickness of the film calculated from the FTIR spectra recorded for 30 different $60\times60\mu\text{m}^2$ areas separated from each other by $300\mu\text{m}$, and distributed along a centered 9 mm segment of the AgLTL sample. The data show that, except few localized defaults, the sample exhibits large homogeneous domain over several millimeters, which is much larger than the size of the pump laser spot in transient absorption experiments (typically $500\mu\text{m}$ diameter). From the intensity of the infrared bands, the calculated average thickness of the sample is 600 nm.

The optical homogeneity of the samples was further characterized by transient absorption measurements using the experimental configuration described in Figure 1. The transmission changes induced by the photoexcitation of AgLTL ($\lambda = 400$ nm, $I = 0.25$ mJcm⁻²) recorded for a series of 20 consecutive measurements, each one consisting of two spectra recorded alternatively at pump-probe delays of -1 ps (baseline recording) and +1 ps (transient spectrum recording), are depicted (Figure 3-c). These repetitive measurements were performed during an overall time period of about 30 min, which corresponds to the typical duration of transient absorption experiments with our setup. During the measurements, the sample AgLTL was continuously displaced in the XZ plane perpendicular to the light propagation. The plotted data highlights three essential points: (i) high quality transient spectra can be recorded at these conditions, thus proving the approachability of the films, (ii) good stability and repeatability of the transient spectra (shape, intensity) along the experiments indicating that the recorded signal is not perturbed neither by the displacement of the sample (spatial homogeneity), nor by the cumulative irradiation time (photostability of the sample), and finally (iii) the flat and stable zero baseline of the transient spectra recorded for the negative pump-probe delay ($\Delta t = -1$ ps) over the entire spectral window shows that the sample recovers its initial state between two consecutive excitation by the laser pump. These results confirm the possible application of nanosized zeolites assembled in films on CaF₂ plates for transient absorption spectroscopy measurements in transmission mode. In the current case, the photoresponse of Ag in the LTL zeolite films was measured.

Hot electrons photodynamics in AgLTL films

The ultrafast photodynamics of the silver NPs in AgLTL films was investigated too. The optical properties of metal nanoparticles with a size less than 20 nm are described by the Mie theory. The absorption cross section of the NPs, ($\sigma_{\text{ext}}(\omega)$), is given by:

$$\sigma_{ext}(\omega) \propto \frac{\omega \epsilon_2(\omega)}{(\epsilon_1(\omega) + 2\epsilon_d)^2 - \epsilon_2(\omega)^2} \quad (1)$$

where, ϵ_d is the static dielectric constant of the medium around the NPs, assumed here real, whereas $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the real and imaginary parts, of the dielectric constant of the metal NPs, respectively. The formation of hot-electrons in the conduction band induces a modification of the dielectric function of the metal and consequently, of the absorption spectrum of the NPs. Hence, the time-evolution of the hot electrons can be followed by transient absorption spectroscopy. The photodynamics of the electrons in silver NPs with different particle sizes have been investigated by this technique previously.^{24–27} So far metal NPs stabilized in zeolites as powders, suspensions and films were not subjected to such characterizations.

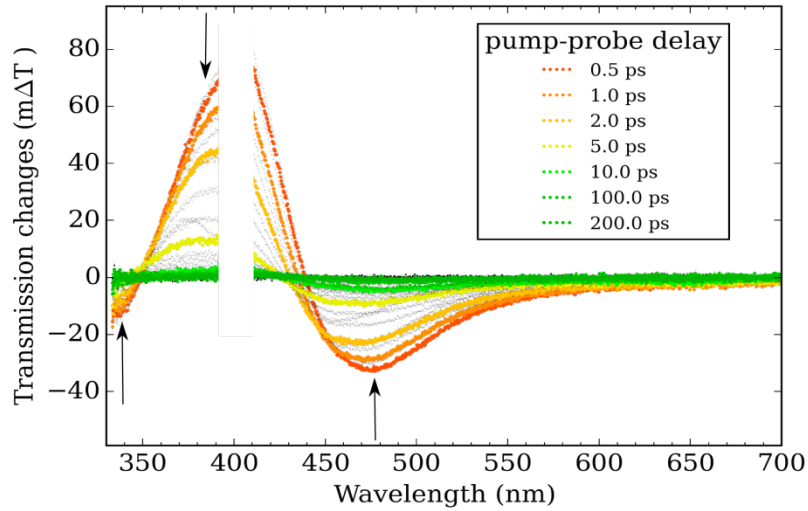


Figure 4 Transient absorption spectra recorded for AgLTL sample upon excitation at 400 nm with a laser intensity of 0.1 mJ cm^{-1}

Typical transient absorption spectra recorded in AgLTL after excitation at 400 nm (pulse intensity $I=0.25 \text{ mJ cm}^{-2}$) for different pump-probe delays are depicted in Figure 4. All spectra exhibit an increase of absorption above the edge of the interband transition (320 nm), and a bipolar-like signal composed by a bleach contribution (420 nm), and an absorption (500 nm) in the red part of the plasmon band. The shape of the transients exhibits the well-known spectral

characteristics and temporal evolution induced by the formation and cooling of hot electrons in silver nanoparticles.^{37,38} The absorption contribution in the blue part of the spectrum is assigned to the presence of new interband transitions resulting from the depletion of the low energy levels of the conduction band. The bipolar contribution is due to the shift and broadening of the plasmon band in response of the redistribution of the electrons inside the conduction band. The transient signal decays within a few picoseconds, that is the typical timescale of the electron-phonon coupling dynamics. Thus, the spectral evolution shown in Figure 4 is undoubtedly assigned to the relaxation of the hot-electrons formed upon the absorption of the laser pump.

To get a better insight into the processes governing this plasmonic response, the temporal evolution of the transient spectra had to be analyzed. According to equation (1), the transient spectra reflect the changes of the dielectric constant of the sample, and therefore the correlation between the measured signal and a microscopic description of the hot-electron dynamics is not straightforward. However, previous investigations²⁴⁻²⁷ have pointed out that for a probe wavelength in the vicinity of the maximum of the bipolar contribution, the real part of the dielectric constant dominates the optical response.³⁷ Therefore, it is possible to establish a relation between the transmission changes and the variation of the internal energy of the electrons (ΔU_e). Using the ratio: $\Delta U_e = C_e \Delta T$, where C_e is the heat capacity of the electrons, the time-evolution of the transmission can be related to the temperature (T_e) of the hot-electron distribution. Moreover, the kinetics of the heat dissipation between the electron (temperature T_e) and the phonons (temperature T_{ph}) of the metal NPs follow the so-called Two-Temperature Model (TTM) described by the following equation:

$$C_e \frac{dT_e}{dt} = -G(T_e - T_l) \quad (2)$$

$$C_l \frac{dT_l}{dt} = G(T_e - T_l) \quad (3)$$

In this equation 2, the TTM expresses the cooling of the hot electrons using the electron-phonon coupling constant $G = 3.5 \times 10^{16} \text{ Wcm}^{-3}\text{K}^{-1}\text{s}^{-1}$ for silver. In equation 3, $C_l = 2.2 \times 10^6 \text{ Jcm}^{-3}\text{K}^{-1}$ is the heat capacity of the silver metal lattice. The heat capacity of the electrons depends on the temperature in the range 1000-7000 K according to the formula: $C_e = \gamma T_e$, where $\gamma = 65 \text{ Jnm}^{-3}\text{K}^{-2}$. Previously, this model was applied successfully to investigate the electron dynamics in silver nanoparticles.^{24–27}

An attractive aspect of the TTM model is that, for a given coupling constant G , the amplitude and the temporal evolution of the decay are fully determined by the initial temperature of the hot-electron ($T_e(0)$) induced by the pump excitation. To compare the photodynamics of AgLTL with the results from the literature, the TTM model was applied to fit the kinetics observed at 380 nm. The fit of the decay ($\lambda_{\text{probe}} = 380 \text{ nm}$) reconstructed from the data presented in Figure 4 is plotted in a linear and semi-log scale (inset) for a comparison (Figure 5). The fit was performed for the pump-probe delays longer than 500 fs, in which case the thermalization of the electrons by electron-electron scattering, and the subsequent establishment of the Fermi distribution do not contribute anymore to the transient signal.³⁷ It can be seen, that the fit reproduces very well the experimental data and notably the specific temporal evolution of the decay associated with the TTM model that is characterized by a progressive acceleration of the temperature decay in the beginning of the process, followed by an asymptotic convergence to the final equilibrium temperature (Figure 5). The fitted value for the initial hot-electron temperature is $T_e(0)=4000 \text{ K}$. Solving the TTM equation also gives the theoretical final equilibrium temperature of the metal at the end of the electron-phonon relaxation. The calculated value is $T_e(>10\text{ps}) = T_{\text{ph}}(>10 \text{ ps}) = 500 \text{ K}$, that represents an ultrafast heating of the metal NPs of about 200 °C above the ambient temperature. In addition, The TTM fit for

several probe wavelengths in the spectral range 370-390 nm was also performed. The results are qualitatively similar, the value of $T_e(0)$ of the TTM varies only within the range 4100-3700 K. To test the sensibility of the model, the same fitting routine was applied using a 2-exponential model but in this case, the data were not reproduced.

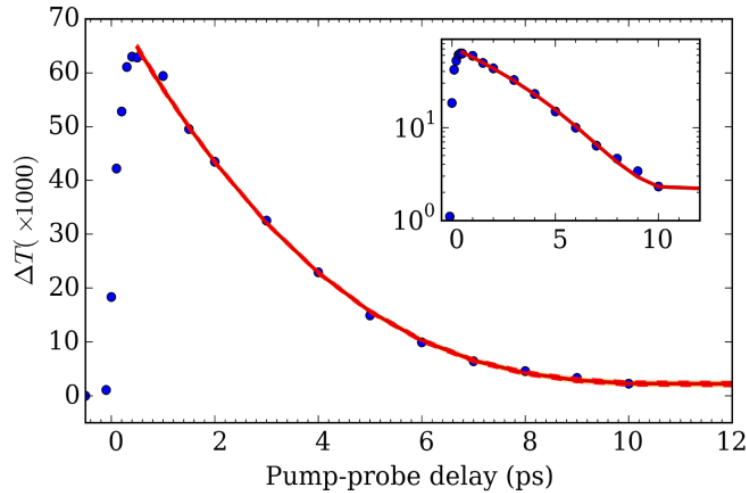


Figure 5 Fit by the TTM model of the kinetics recorded at 380 nm upon excitation of AgLTL at 400 nm with a laser intensity $I = 0.25 \text{ mJcm}^{-2}$. The fit curve in red has been obtained for an initial electronic temperature $T_e(0) = 4100 \text{ K}$. The dotted curves show 95% confidence interval of the fit. Inset: experimental data and the fit plotted in a semi-log scale

The value of the initial hot electrons temperature of 4100 K obtained from the above fit is compared with the theoretical value calculated from the energy absorbed by the Ag NPs in the AgLTL. If we assume that the totality of the energy of the photons absorbed by a NP is converted into internal energy of the hot-electrons, then the temperature of the hot-electrons distribution $T_e(0)$ is given by equation 5 that depends only on the number of photons (n) adsorbed within the volume (V) of the nanoparticle.

$$T_e = \sqrt{T_l^2 + 2 \frac{nhc}{V\lambda\gamma}} \quad (5)$$

Given the excitation conditions of the spectra in Figures 4 and 5 and using the $\sigma = 1.5 \cdot 10^{-17} \text{ cm}^2$ of the absorption cross-section of a silver atom, the numerical application predicts that, in our experiments, less than 1 photon per 300 silver atoms is absorbed. On this basis, the initial electronic temperature was calculated for the different classes of NP presented in the histogram in Figure 2, and using this yield of absorption of 1 photon/300 silver atoms. From the NPs size

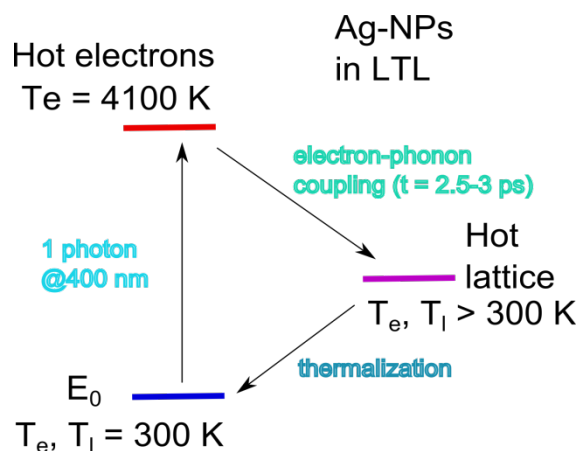
distribution (Figure 2), we deduced the probability (P) that a photon is absorbed by the NPs of a given size in AgLTL, and finally estimated the relative contributions of the different populations of particle sizes to the transient absorption signal by assuming these contributions proportional to $P \times T_e^2$. The results are reported in Table 1.

Table 1 Calculated initial electronic temperature ($T_e(0)$), probability that a photon is absorbed by a NP (P), and total contribution (Contrib) of a NP population to the overall transient absorption signal, as a function of the particle size. ^{a)} For this very small size T_e is overestimated because the relationship $C_e = \gamma T_e$ is not valid anymore. ^{b)} The contribution to the transient signal is calculated for the lowest temperature T_e of a given class of particles. ^{c)} These values correspond to the absorption of a single photon/NP

NP Diameter	Number of atoms	$T_e(0)$	P	Contrib ^{b)}
(nm)	-	(Kelvin)	(Norm.)	(%)
0.5 -1.1	13-55	>7000 ^{a)} -5725	0.05	31
1.1-1.6	55-147	5725-2900	0.12	24
1.6-2.2	147-309	2900-1900	0.19	15
2,2-2.75	309-561	1900-1378	0.22	9.5
2,75-3.3	561-923	1378-1477 (-xx) ^{c)}	0.17	9
3.3-3.8	923-1415	1477-1438 (-xx)	0.18	9
3.8-5	1415-2869	1438-2000 (-xx)	0.04	3

The NPs with sizes 0,5-2.2 nm contribute roughly to 70% of the initial transient signal, with an initial electronic temperature $T_e(0) = 5725-1900$ K . Although quite approximate, this theoretical initial electronic temperature based on the optical properties of Ag NPs and on the HRTEM particle size distribution is in reasonably good agreement with the value deduced from the fit of the experimental transient data using the TTM model. Hence, the dynamics behind the transient data can be assigned to the formation of a highly excited hot-electron distribution that relax mainly by electron-phonon coupling as illustrated in Scheme 1. It can also be concluded that the initial temperatures calculated (Table 1), and the distribution of the absorbed

photons based on the particles size distribution can be used to predict the plasmonic behavior of AgLTL.



Scheme 1 Plasmonic photodynamics in the AgLTL film

Based on the plasmonic behavior of the AgLTL, the following conclusions are made: (i) the metallic character of the nm-sized silver NPs formed on LTL nanosized zeolites is preserved, in the sense that the hot-electrons remain localized into the Ag NPs and (ii) their dynamics is, apparently, not strongly affected by the LTL framework. This is an important characteristic of the AgLTL materials, notably in view of plasmonic chemistry applications. It is worth to point out that these properties are far from being evident or even predictable without the experimental results described here. Indeed, when metal NPs are in contact with a surrounding media, electronic interactions can influence severely the optical plasmonic response^{39–41} and the dynamics of the hot-electrons.^{26,28} In extreme cases, the electrons of the metal can be photoinjected inside the support, and the plasmonic character lost.⁴² So, the role of the NP-support interactions is crucial in determining the plasmonics chemistry properties of a material. Zeolites are concerned with this potential issue. Recent theoretical calculations have shown that the vacant orbitals of the oxygen atoms constituting the zeolite framework are lying closely above the Fermi level of silver NPs.⁴³ Therefore, these orbitals can act as accepting energy levels for the hot-electrons and might potentially affect the plasmonic properties of silver-containing zeolites. Here, by transient absorption spectroscopy, we demonstrate that the

coupling between the Ag NPs and the zeolite framework is not effective, and it can be considered that the NPs behave essentially as free supported NPs.

A second major result demonstrated by the analysis of the transient data is that, due to the small Ag NP size (less than 2.5 nm), a highly excited hot-electrons distribution, characterized by an initial electron temperature above 2000 K, is generated in the major cases by the absorption of a single photon by each Ag NPs. This implies that the reactive state can be populated under monophotonic excitation conditions, and particularly under solar illumination. In addition, the process of excitation is efficient, as we estimate the yield of absorption of a photon by the smallest Ag NPs (< 2.5 nm) is higher than 30% (Table 1).

Conclusions

In this work, for the first time the potential of using silver containing nanosized zeolites for hot-electrons driven chemistry applications has been considered. This issue has been addressed by investigating the ultrafast optical response of the materials photo-excited in resonance with the plasmon band of the Ag NPs. The preparation of Ag NPs highly dispersed in nanosized LTL type is presented, followed by their immobilization in films. For the pump-probe experiments, the silver containing nanosized zeolites were assembled as transparent layers on CaF₂ plates. This is the first report on transient absorption measurements performed in zeolite films. It has been shown that reliable transient spectra can be obtained under controlled atmosphere, and authors believe that beyond the scope of the work, the experimental approach described in the report is promising to investigate the host-guest photoreactivity in zeolites. These transparent films are also well adapted for being engineered as optical devices.

It is demonstrated that the zeolite nanocrystals stabilized very small silver NPs without perturbing their electronic properties, and therefore they behave as free Ag NPs. It is also demonstrated that these materials can be potentially highly photoactive under solar illumination conditions owing to the possible formation of hot-electrons with a high initial electronic

temperature by the absorption of a single photon per NP. In summary, these results reveal the high potential of Ag containing LTL nanosized zeolites for plasmonic chemistry applications.

References

- 1 K. Watanabe, D. Menzel, N. Nilius and H. Freund, *Chem. Rev.*, 2006, **106**, 4301–4320.
- 2 G. Baffou and R. Quidant, *Chem. Soc. Rev.*, 2014, **43**, 3898–907.
- 3 P. Zhang, T. Wang and J. Gong, *Adv. Mater.*, 2015, **27**, 5328–5342.
- 4 J. Y. Park, S. M. Kim, H. Lee and I. I. Nedrygailov, *Acc. Chem. Res.*, 2015, **48**, 2475–2483.
- 5 X. Y. Liu, A. Wang, T. Zhang and C. Y. Mou, *Nano Today*, 2013, **8**, 403–416.
- 6 X. Zhang, X. Ke, A. Du and H. Zhu, *Sci. Rep.*, 2014, **4**, 3805.
- 7 X. Zhang, X. Ke and H. Zhu, *Chem. - A Eur. J.*, 2012, **18**, 8048–8056.
- 8 S. Mintova, M. Jaber and V. Valtchev, *Chem. Soc. Rev.*, 2015, **44**, 7207–7233.
- 9 T. Bein and S. Mintova, *Zeolites and Ordered Mesoporous Materials: Progress and Prospects*, Elsevier, 2005, vol. 157.
- 10 H. Awala, J.-P. Gilson, R. Retoux, P. Boullay, J.-M. Goupil, V. Valtchev and S. Mintova, *Nat. Mater.*, 2015.
- 11 E.-P. Ng, D. Chateigner, T. Bein, V. Valtchev and S. Mintova, *Science (80-.)*, 2012, **335**, 70–73.
- 12 G. Majano, L. Delmotte, V. Valtchev and S. Mintova, *Chem. Mater.*, 2009, **21**, 4184–4191.
- 13 G. Majano, S. Mintova, O. Ovsitser, B. Mihailova and T. Bein, *Microporous Mesoporous Mater.*, 2005, **80**, 227–235.
- 14 M. Hözl, S. Mintova and T. Bein, *Stud. Surf. Sci. Catal.*, 2005, **158**, 11–18.
- 15 J. Kobler, H. Abrevaya, S. Mintova and T. Bein, *J. Phys. Chem. C*, 2008, **112**, 14274–14280.
- 16 S. Mintova, M. Jaber and V. Valtchev, *Chem. Soc. Rev.*, 2015, **44**, 7207–7233.
- 17 A. Souici, K.-L. Wong, V. De Waele, J. L. Marignier, T. H. Metzger, N. Keghouche, S. Mintova and M. Mostafavi, *J. Phys. Chem. C*, 2014, **118**, 6324–6334.
- 18 K.-L. Wong, A. Souici, V. De Waele, M. Mostafavi, T. H. Metzger and S. Mintova, *Langmuir*, 2010, **26**, 4459–64.
- 19 I. Yordanov and R. Knoerr, *J. ...*, 2010, 20974–20982.
- 20 R. Knoerr, I. Yordanov, V. De Waele, S. Mintova and M. Mostafavi, *Sens. Lett.*, 2010, **8**, 497–501.
- 21 F. Luchez, Z. Tahri, V. De Waele, I. Yordanov, S. Mintova, A. Moissette, M. Mostafavi and O. Poizat, *Microporous Mesoporous Mater.*, 2014, **194**, 183–189.
- 22 B. Dong, S. Belkhair, M. Zaarour, L. Fisher, J. Verran, L. Tosheva, R. Retoux, J.-P. Gilson and S. Mintova, *Nanoscale*, 2014, **6**, 10859–10864.
- 23 J. Kecht, Z. Tahri, V. De Waele, M. Mostafavi, S. Mintova and T. Bein, *Chem. Mater.*, 2006, **18**, 3373–3380.
- 24 S. Link and M. A. El-Sayed, *J. Phys. Chem. B*, 1999, **103**, 8410–8426.
- 25 N. Del Fatti, C. Voisin, M. Achermann, S. Tzortzakis, D. Christofilos and F. Vallée, *Phys. Rev. B*, 2000, **61**, 16956–16966.
- 26 J. Bigot, V. Halte, J. Merle and A. Daunois, 2000, 181–203.
- 27 G. V Hartland, *Chem. Rev. (Washington, DC, U. S.)*, 2011, **111**, 3858–3887.
- 28 C. Bauer, J. P. Abid and H. H. Girault, *Chem. Phys.*, 2005, **319**, 409–421.
- 29 M. Bonn, M. J. P. Brugmans, A. W. Kleyn and R. A. van Santen, *Chem. Phys. Lett.*, 1995, **233**, 309–314.
- 30 G. Flachenecker and A. Materny, *J. Chem. Phys.*, 2004, **120**, 5674–5690.
- 31 M. Gil, M. Ziólek, J. A. Organero and A. Douhal, *J. Phys. Chem. C*, 2010, **114**, 9554–9562.
- 32 N. Alarcos, B. Cohen and A. Douhal, *J. Phys. Chem. C*, 2014, **118**, 19431–19443.

- 33 K. S. Kumar, S. T and P. Natarajan, 2011, **126**, 945–954.
- 34 U. Schmidhammer, V. De Waele, S. Mintova, E. Riedle and T. Bein, *Adv. Funct. Mater.*, 2005, **15**, 1973–1978.
- 35 T. Bein, 2004, 10640–10648.
- 36 G. Buntinx, R. Naskrecki and O. Poizat, *J. Phys. Chem.*, 1996, **100**, 19380–19388.
- 37 C. Voisin, C. Voisin, N. Del Fatti, N. Del Fatti, D. Christofilos, D. Christofilos, F. Vallée and F. Vallée, *J. Phys. Chem. B*, 2001, **105**, 2264–2280.
- 38 J. H. Hodak, I. Martini and G. V. Hartland, *J. Phys. Chem. B*, 1998, **102**, 6958–6967.
- 39 H. Hovel, S. Fritz, A. Hilger, U. Kreibig and M. Vollmer, *Phys. Rev. B*, 1993, **48**, 18178–18188.
- 40 U. Kreibig, *Appl. Phys. B Lasers Opt.*, 2008, **93**, 79–89.
- 41 A. Y. Stakheev and L. . Kustov, *Appl. Catal. A Gen.*, 1999, **188**, 3–35.
- 42 E. Khon, A. Mereshchenko, A. N. Tarnovsky, K. Acharya, A. Klinkova, N. N. Hewa-Kasakarage, I. Nemitz and M. Zamkov, *Nano Lett.*, 2011, **11**, 1792–1799.
- 43 S. G. Chiodo and T. Mineva, *J. Phys. Chem. C*, 2016, **120**, 4471–4480.

Appendix

Film thickness determination by FTIR spectroimaging

The intensity of the zeolite framework vibration (integrated area between 1304 and 941 cm^{-1}) is used to quantify the thickness of the film. The linear correlation between the area of the band and the thickness was determined using a LTL film deposited on a silicon wafer. Figure SI-1 shows the optical image (A) On the optical image (A), the top of the picture corresponds to the uncovered Si surface and the LTL film is on the bottom. The FTIR spectra were recorded for the spatial area corresponding to the optical image with a spatial resolution of $1.1 \times 1.1 \mu\text{m}^2$ per pixel. An example of recorded spectrum is given in Figure 1. The most intense band (in grey) corresponds to the zeolite framework vibration. In Figure1-C the IR image was reconstructed by integrating the IR spectra in the range of 1304-941 cm^{-1} for each measured pixel.

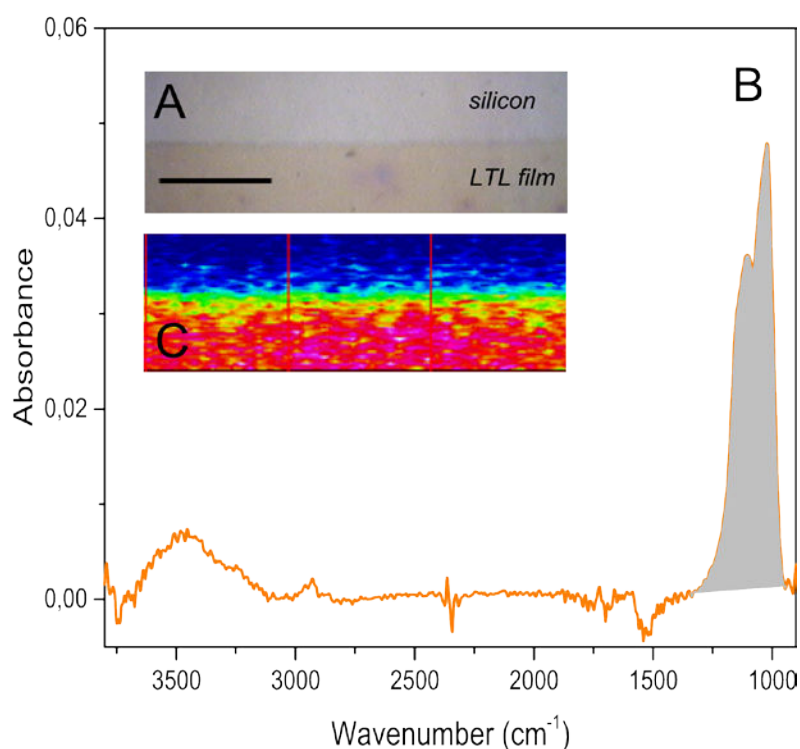


Figure-SI-1 (A) Optical image of a LTL on Si, (B) Representative infrared spectra of the zeolite film and (C) 2D Map of the integrating absorbance of the zeolite band between 1304 and 941 cm^{-1} . In image C, the color varies from blue-to-red as the intensity of the IR band increases.

For the FTIR image, the distribution of the intensity of the zeolite band was analyzed (Figure SI-2 A), and the average value was determined: $I = 8.1$. The film thickness was measured by

SEM imaging (fig SI-2 B). So, the calibration is: Integrated intensity of zeolite framework band
 $= 3.2 / 100 \text{ nm}$ (thickness of the film) This factor was applied to determine the thickness of
 AgLTL film.

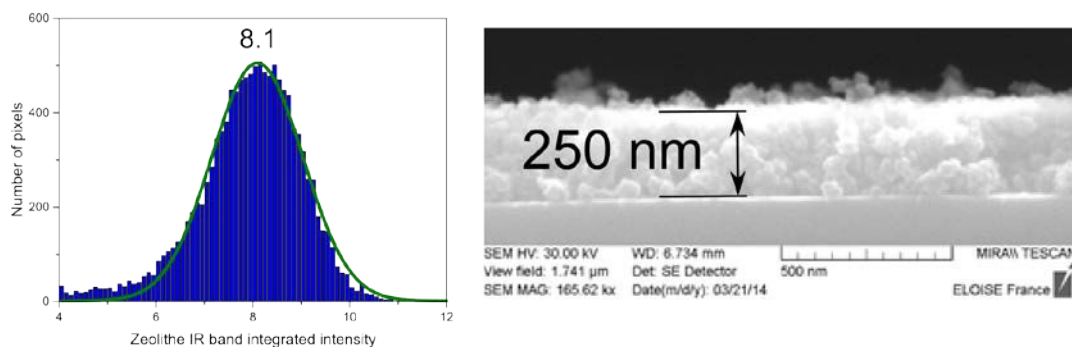


Figure SI-2 (Histogram showing the number of detector pixels for the different values of the Integrated intensity of the zeolite band between 1304 and 941 cm^{-1} (in green, the Gaussian fit of the curve) and SEM image of the film.

Complementary fits by the TTM model

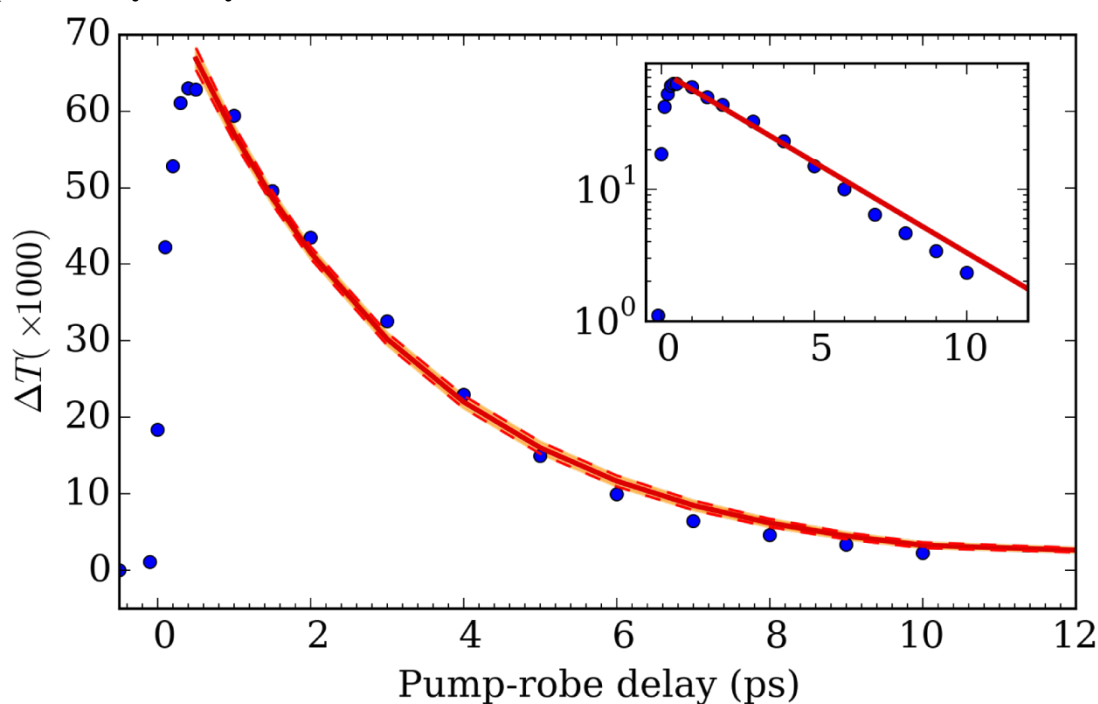


Figure SI-3 Fit of the decay of the transient signal (380 nm) using a 2 exponential model. The fit is not satisfactory

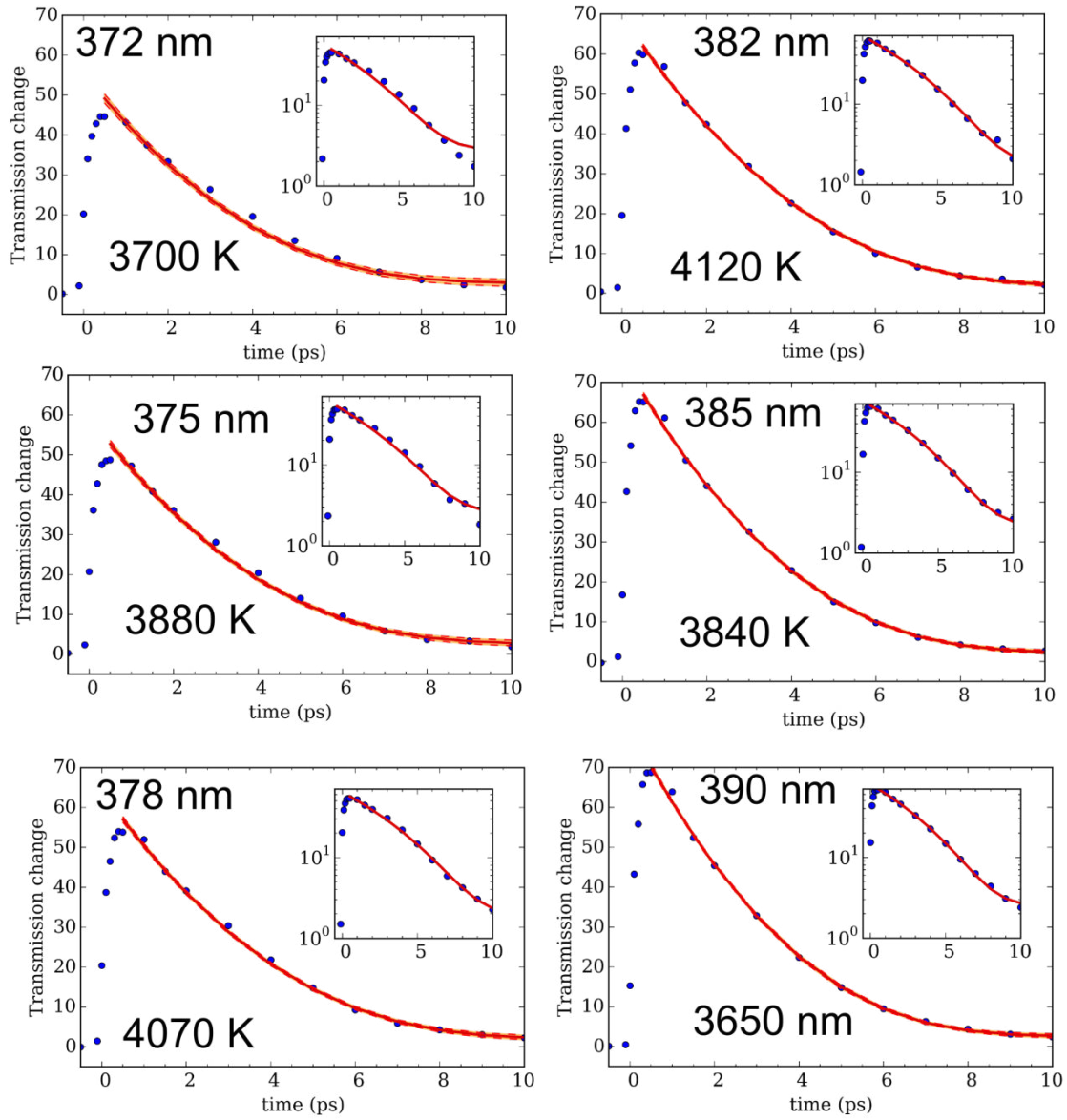


Figure SI-4 Fit of the decay of the transient signal using the TTM model for different probe wavelength in the range 372-390 nm. The fitted temperature value ($T_e(0)$) varies in the range 3650 - 4070 Kelvins

General Conclusions

This manuscript has combined all stages from the preparation of copper containing LTL zeolites to their possible applications. The synthesis and characterization protocols allow to control the particle size, shape, and morphology of the materials, as well as the state of the copper species in the zeolite matrix, which is of paramount importance in the development of advanced nanomaterials. The properties of the Cu containing LTL zeolites are tailored and thus the applications in sensing, selective adsorption on metals and photo catalysis were explored. Within this work, the effect of the preparation conditions on the state of copper in the nanosized zeolite matrix was studied in detail. The main experimental methods applied are powder X-ray diffraction, in situ IR spectroscopy using probe molecules, UV-vis spectroscopy, nitrogen sorption, scanning and transmission electron microscopies.

The most important findings in this study can be summarized as follows.

1. A detailed study of the evolution of copper species in the LTL nanosized zeolite suspension reduced with hydrazine revealed the formation of copper nanoparticles with dimensions limited by the size of the LTL zeolite channels and cages. However, with prolonged reduction time, the Cu NPs tend to migrate to the zeolite surface due to their high mobility in aqueous media, resulting in large copper particles. Transmission electron microscopy shows the presence of 0.2-1.6 nm Cu NPs distributed throughout the zeolite crystals after 190 min chemical reduction. After 280 min, there are more Cu NPs formed within the zeolite pores and on their surface with a maximum size of 2.2 nm. Finally, larger copper nanoparticles were formed on the zeolite surface, while the LTL zeolite structure was completely preserved.
2. The reduction of copper in zeolite matrix results in a complex system, containing different copper species: residuals of Cu^{2+} , Cu^+ , and CuNPs. The results of FTIR

spectroscopy show the heterogeneity of Cu^{2+} and Cu^+ cations in the Cu-LTL zeolite prepared by ion-exchange approach. Furthermore, the quantitative analysis based on CO adsorption followed by FTIR shows that the relative amount of copper in (1+) state is ~30%. This agrees with the amount of CuNP determined by UV-Vis measurements (56%).

3. The state and behavior of copper in the LTL zeolite strongly depend on the method used for the Cu inclusion. The copper introduced by in situ synthesis approach shows distinct environment and occupies different position compared to the Cu introduced by ion exchange method. The ion exchange approach leads to modifications of the samples causing the displacement of a significant amount of Cu to the extra-framework positions, as has been revealed by adsorbing various probe molecules.
4. The suspensions of copper-containing LTL zeolite were assembled in thin films on silicon wafers and CaF_2 plates via spin-coating approach. The films with different thickness, mechanical and chemical stability were obtained by adjusting the deposition parameters and using organic binders. The films were further employed for detection of low concentration of CO at ambient temperature. The copper-containing zeolite films demonstrate high sensitivity and fast response toward low concentrations of CO (1-100 ppm).
5. The ion exchange procedure was applied to prepare silver containing LTL type zeolite nanocrystals. The potential of using the silver containing nanosized zeolites for hot-electrons driven chemistry applications has been demonstrated. The ultrafast optical response of the Ag-LTL nanocrystals photo-excited at the plasmon band of the Ag NPs was studied. In addition, the Ag-LTL nanocrystals were assembled as transparent layers on CaF_2 plates. The first transient absorption measurements performed on Ag-LTL zeolite films were performed. It has been shown that reliable transient spectra can be

obtained under controlled atmosphere. It has been demonstrated that the zeolite nanocrystals stabilized very small silver NPs without perturbing their electronic properties, and therefore they behave as free Ag NPs. It is also demonstrated that these materials can be potentially highly photoactive under solar illumination conditions owing to the possible formation of hot-electrons with a high initial electronic temperature by the absorption of a single photon per Ag NP.

Although the important results on the copper-containing nanozeolites have been achieved in the present work in terms of the kinetics of the Cu NPs growth and characterization of the copper species introduced to the zeolite host by different approaches, there are still many challenges to be addressed. In particular, the stability issues of Cu NPs and their tendency to migrate from the zeolite matrix with time to form bulk particles, especially under harsh conditions have to be studied.

The results obtained reveal the high potential of metal containing LTL nanosized zeolites for plasmonic chemistry applications. However, the structural transformations occurring during the photocatalytic reaction require special attention, and it is prudent to characterize the materials after photocatalytic tests and compare with the as-prepared materials to precisely elucidate and identify the active catalytic sites. In situ and operando spectroscopy are ideal tools for observation of the possible structural variation of the Cu species during catalytic processes.

Résumé

Les objectifs principaux de ce travail étaient d'étudier la nature des composés de cuivre formés dans les nano-zéolithes en utilisant deux approches: (i) incorporation directe du Cu via une synthèse mono pot et (ii) incorporation post-synthèse du Cu suivi par une réduction chimique.

Une étude détaillée de l'évolution des espèces de cuivre dans la suspension de nano-zéolithe LTL réduite avec de l'hydrazine a révélé la formation de nanoparticules de cuivre avec des dimensions limitées par la taille de canaux et des cages de la zéolithe. Cependant, avec un temps de réduction prolongé, les NPs de Cu ont tendance à migrer vers la surface de la zéolithe en raison de leur forte mobilité dans les milieux aqueux, et donne lieu à de grosses particules de cuivre, tout en conservant la structure de la zéolithe. La réduction du cuivre donne lieu à un système complexe contenant différentes espèces de cuivre: des résidus de Cu^{2+} , Cu^+ et des NPs de Cu. Les études par spectroscopie IRTF montrent l'hétérogénéité des cations Cu^{2+} et Cu^+ dans la zéolithe Cu-LTL préparée par échange ionique. Il a été prouvé, que l'état et le comportement du cuivre dans la zéolithe LTL dépendent fortement de la méthode utilisée pour l'incorporation du Cu, soit par échange ionique, soit par incorporation directe du Cu. Il est devenu évident que le cuivre ajouté au mélange de synthèse possède un environnement distinct et occupe une position différente quand il est comparé à celui de l'échange ionique. Il est vraisemblablement partiellement localisé dans la charpente zéolithique ou /caché dans la structure et est inaccessible pour les molécules adsorbées. De plus, les modifications post-synthèse du matériau obtenu par synthèse directe entraînent un déplacement vers des positions hors structure d'un nombre important de Cu. De plus, les films minces de zéolithes contenant du métal avec des épaisseurs différentes ont été obtenue par un procédé de revêtement par centrifugation de supports de silicium et/ou des supports optiques CaF_2 . Ce dernier a été utilisé pour la détection de CO en faible concentration à température ambiante et l'étude de la réponse optique ultrarapide du matériau photo-excité en résonance avec la bande du plasmon des NPs métalliques. En résumé, ce travail couvre entièrement toutes les étapes de la synthèse, la modification, la caractérisation complète et l'utilisation de nano-cristaux de zéolithe contenant du métal. La combinaison des propriétés uniques des nanoparticules de cuivre et de la polyvalence des nano-zéolites donne lieu à des matériaux avancés intéressants pour de nombreuses d'applications dans des dispositifs de taille nanométrique, la détection sélective de produit chimique, la catalyse, etc.

Mots clés: Zéolites; Cuivre; Nanoparticules de cuivre, Spectroscopie femtoseconde, Spectroscopie infrarouge à transformée de Fourier; Spectroscopie ultraviolette sous vide, Couches minces

Abstract

The main objectives of this work were to study the nature of copper species formed in the nanosized zeolites using two approaches: (i) direct incorporation of Cu via one pot synthesis, and (ii) post synthesis incorporation of Cu followed by chemical reduction. A detailed study of the evolution of copper species in the LTL nanosized zeolite suspension reduced with hydrazine revealed the formation of copper nanoparticles with the dimensions limited by the size of zeolite channels and cages. However, with prolonged reduction time, the Cu NPs tend to migrate to the zeolite surface due to their high mobility in aqueous media, resulting in large copper particles, while the zeolite structure is preserved. The reduction of copper resulted in a complex system, containing different copper species: residuals of Cu^{2+} , Cu^+ , CuNPs. The results of FTIR spectroscopy show the heterogeneity of Cu^{2+} and Cu^+ cations in the Cu-LTL zeolite prepared by ion-exchange procedure. It has been proven, that the state and behavior of copper in LTL zeolite strongly depend on the method used for Cu inclusion: ion exchange or direct Cu incorporation. It became evident, that copper added to the synthesis mixture shows distinct environment and occupies different position when compared to ion exchange. It is presumably partially located in the zeolite framework or occluded in its walls and is inaccessible by adsorbed molecules. In addition, the post-synthesis modifications of the material obtained by direct synthesis cause the displacement of a significant amount of Cu to the extra-framework positions. Further, the metal containing zeolite thin films with different thickness were obtained by spin-coating approach on silicon wafers and CaF_2 optical plates. The latter were after employed for detection of low concentration of CO at ambient temperature and investigation of the ultrafast optical response of the materials photo-excited in resonance with the plasmon band of the Me NPs. In summary, the present PhD thesis fully covers the all steps from the synthesis, modification, thorough characterization, and application of metal-containing nanosized zeolite crystals. The combination of unique properties of copper nanoparticles with versatility of nanozeolites give rise to the development of advanced materials which are interesting for many applications in nanoscale devices, selective chemical sensing, catalysis etc.

Keywords: Zeolites; Copper; Copper nanoparticles; Femtosecond spectroscopy; Fourier transformed infrared spectroscopy; Ultraviolet-visible spectroscopy; Thin films