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Mesoporous MEL, BEA, and FAU zeolite crystals obtained by in-situ formation of carbon template over metal nanoparticles

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Here, we report the synthesis and characterization of hierarchical zeolite materials with MEL, BEA and FAU structures. The synthesis is based on the carbon templating method with an in-situ-generated carbon template. Through the decomposition of methane and deposition of coke over nickel nanoparticles supported on silica, a carbon-silica composite is obtained and exploited as a combined carbon template/silica source for the zeolite synthesis. The mesoporous zeolite materials were all prepared by hydrothermal crystallization in alkaline media followed by removal of the carbon template by combustion, which results in zeolite single crystals with intracrystalline pore volumes of up to 0.44 cm³/g. The prepared zeolite structures are characterized by XRD, SEM, TEM and N₂ physisorption measurements.

1 Introduction

Zeolites are crystalline inorganic materials with an ordered microporous structure and strong acid sites that are extensively used as heterogeneous catalysts in oil refining and chemical synthesis [1, 2]. Furthermore, zeolites possess high surface areas and large pore volumes and are therefore used in many modern industrial processes related to catalysis, adsorption, and separation, where they provide excellent size- and shape-selectivity [3, 4]. However, the large-scale application of zeolites has still not reached its full potential [5], because zeolite catalysts often suffer from severe diffusion limitations. Since the reactants and products have to diffuse through the micropores in order to reach and leave the active sites, the diffusion in zeolites is often orders of magnitude slower than both molecular and Knudsen diffusion. These diffusion limitations are enhanced for large and bulky compounds that closely match the pore sizes of the zeolites and will inevitably slow down the reaction rate.

Moreover, in some reactions, coke formation enhances these limitations, as the coke deposits block the zeolite micropores, which results in a rapid decrease in catalytic activity [6, 7]. Therefore, several preparative strategies have been developed in the attempt to improve the performance of zeolites in catalysis: the synthesis of zeolites with extra-large pores [8-11], direct synthesis of zeolite nanocrystals [12-17], by exfoliating layered zeolites [18, 19], and by introducing mesopores in the microporous materials through templating strategies [7, 20-22] or demetallation processes [4, 7, 23-25]. Recently, a novel synthesis procedure for the preparation of mesoporous MFI-type material based on the carbon templating method with an in-situ-generated carbon template was reported by our group [26]. The mesoporous zeolite crystals combine the shape-selectivity, hydrothermal stability, and high acidity typical for conventional zeolites with highly efficient transport of reactants and products typical for mesoporous materials [7]. The novel synthesis approach has several advantages in comparison with existing carbon templating methods, where relatively complicated preparative strategies involving multistep impregnation procedures are used [27-30]. In the presented approach a cheap and available silica source - silica gel (SiO₂) is used. The carbon template is generated in situ by decomposition of methane, which results in the formation of large amounts of coke around the silica supported nickel nanoparticles [26]. The formation of coke over metal nanoparticles is a well-known phenomenon for a range of catalytic reactions that is frequently investigated [31]. For the decomposition of methane, supported nickel nanoparticles are recognized as effective catalysts [32]. In this way, the novel synthesis approach is more cost effective in comparison with the conventional carbon templating approach that relies on relatively expensive starting materials such as carbon black pearls and tetraethyl orthosilicate [7, 27, 28, 30]. The encapsulated carbon is removed by combustion after the zeolite crystallization, which creates mesoporosity in the zeolite crystals. In Fig. 1 a schematic overview of the presented synthesis approach is given.

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Further, the mesoporous zeolites were characterized using X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) to study the in-situ generated carbon template. The XRD patterns showed the presence of the FAU structure in the mesoporous zeolites, indicating the presence of the desired acidity. TEM images revealed the presence of nickel nanoparticles on the surface of the mesoporous zeolites, indicating the successful incorporation of nickel into the zeolite framework.

2.6 Zeolite Synthesis

2.6.1 Preparation of Ni-containing silica-carbon composite material. The silica-carbon composite was prepared according to the following procedure. A 0.15 g of Ni(NO₃)₂·6H₂O was dissolved in 1.73 g of water. The mixture was stirred until a clear solution was obtained. Then, 1.50 g of SiO₂ was impregnated with this solution. The mixture was heated at 140 °C and kept there for 24 h. The nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma-Aldrich) and methanol gas (CH₃OH, AGA), forming gas (10% H₂/N₂, AGA), argon gas (Ar, AGA) and distilled water were used.

2.6.2 Synthesis of Ni-containing mesoporous MEL-type zeolite. The mesoporous Ni-containing Na-ZSM-11 material was prepared according to the following procedure. In a 100 ml flask, 3.16 g of H₂O, 0.14 g of NaOH and 0.21 g of NaAlO₂ were added with stirring until a clear solution was obtained. Then, 3.18 g of TBAOH was added to this mixture. The resulting solution was stirred at 175 °C and kept there for 24 h. The autoclave was cooled to room temperature, the product was washed with deionized water, and the carbon was removed by controlled combustion in air in a muffle furnace at 550 °C for 15 h.

2.6.3. Synthesis of Ni-containing mesoporous BEA-type zeolite. The mesoporous Ni-containing Na-Beta material was prepared according to the following procedure. In a 100 ml flask, 0.08 g of NaOH, 1.74 g of H₂O, 0.17 g of NaAlO₂ and 4.25 g of TEAOH were added with stirring until a clear solution was obtained. After that, the Ni-containing silica-carbon composite obtained above (2.6.1) was impregnated with this mixture. The Ni-containing silica-carbon composite was then subjected to 175 °C and kept there for 2 h. Then, the autoclave was cooled to room temperature, the product was washed with deionized water, and the carbon was removed by controlled combustion in air in a muffle furnace at 550 °C for 16 h.

2.5 Materials

All reagents were of reagent grade and used without further purifications: tetrabutylammonium hydroxide (TBAOH, 40 wt%, Sigma-Aldrich), tetraethylammonium hydroxide (TEAOH, 35 wt%, Sigma-Aldrich), silica gel (SiO₂, Davisil Grade 62, pore size 150 Å, 60-200 mesh, Sigma-Aldrich), sodium hydroxide (NaOH, 97%, VWR), sodium aluminate (NaAlO₂, 54 wt % Al₂O₃ and 41 wt % Na₂O, Riedel-de Haen), aluminium nitrate (Al(NO₃)₃·9H₂O, Riedel-de Haen), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma-Aldrich), methane gas (CH₄, AGA), forming gas (10% H₂/N₂, AGA), argon gas (Ar, AGA) and distilled water.
l) and filtered by suction. The zeolite was dried at 90°C for 10 h, and the organic template and the carbon were removed by controlled combustion in air in a muffle furnace at 550°C for 24 h.

2.6.4. Synthesis of Ni-containing mesoporous FAU-type zeolite. The synthesis of mesoporous FAU-type crystals was based on the recipe from the patent by Christensen et al. Example 9 [34]. In a typical synthesis procedure, the freshly prepared chemicals were used: sodium silicate (200 g/l SiO₂), sodium aluminate solution (240 g/l Al₂O₃), sodium hydroxide solution (400 g Na₂O/l). The mesoporous NaY material was prepared using seed gel according to the following procedure. Seed gel was made by the followed recipe: in 100 ml flask 9.3 ml of sodium aluminate solution (240 g/l Al₂O₃), 19.97 ml of sodium hydroxide solution (400 g/l Na₂O) and 50 ml of sodium silicate (200 g/l SiO₂) were added slowly with stirring. After that the mixture was left for 4 hours. Synthesis gel was prepared by the followed procedure: in 100 ml flask 4.4 ml of sodium aluminate solution (240 g/l Al₂O₃), 2.35 ml of sodium hydroxide solution (400 g/l Na₂O) and 5.46 ml of sodium silicate (200 g/l SiO₂) were added slowly with stirring. After that, the Ni-containing silica-carbon composite obtained above (2.6.1) and 0.48 ml of seed gel was added slowly. The mixture was left for 1 hour with stirring. The composition of the resulting synthesis gel was 1 Al₂O₃ : 7 SiO₂ : 5 Na₂O : 85 H₂O. Then the gel was introduced into a stainless steel autoclave, containing 15 g of water to produce saturated steam, heated to 100°C and kept there for 18 h. Then, the autoclave was cooled to room temperature, the product was washed with deionized water (1L) and filtered by suction. The zeolite was dried at 90°C for 10 h, and the carbon template was removed by controlled combustion in air in a muffle furnace at 550°C for 24 h.

2.6.5. Synthesis of reference conventional zeolite materials. All conventional materials MEL, BEA and FAU were synthesized the same way as the corresponding mesoporous materials using 1.5 g of pure SiO₂ instead of the Ni-containing silica-carbon composite described above (2.6.1).

3. Results and Discussion

All X-ray powder diffraction (XRPD) patterns were obtained after the zeolite synthesis and subsequent combustion of the organic template and/or the carbon material. XRPD patterns for the conventional- and mesoporous ZSM-11, Beta and Zeolite Y zeolites are shown in Fig. 2. Based on these data, all obtained zeolites are concluded to be highly crystalline structured materials.
Representative results of SEM for the conventional and mesoporous ZSM-11, Beta and Zeolite Y zeolites after combustion of the carbon template are shown in Fig. 4. From the SEM images it can be seen that all samples are highly crystalline and that crystals of uniform size are obtained. The average crystal size of both conventional and mesoporous zeolites determined from SEM images in Fig. 4 and are about 3 \( \mu m \) for ZSM-11, 1 \( \mu m \) for Beta and 0.5 \( \mu m \) for Zeolite Y.

The major difference between the conventional and mesoporous ZSM-11 and Beta zeolite crystals, is the presence of non-crystallographic intracrystalline mesopores resulting in the high porosity. The conventional zeolite ZSM-11 has the typical coffin-shape intergrown crystals, and the conventional Beta material has the typical rounded-cube shape. From the SEM images of the mesoporous ZSM-11 and Beta zeolites, it can be seen that the crystals have shapes typical for the mesoporous single crystals. The conventional and mesoporous crystals of Zeolite Y materials look very similar due to rather moderate degree of mesoporosity in the mesoporous sample.
Ni-Beta nanoparticles could find use in industrial applications. Thus, with this novel and simple preparation method, it will be possible to obtain mesoporous zeolite Beta in alkaline media.

In conclusion, the preparation of mesoporous ZSM-11, Beta and Y-type zeolite single crystals modified with Ni-nanoparticles based on the carbon templating method with an in-situ-generated carbon template is reported for the first time. The obtained zeolite materials combine high crystallinity with an intracrystalline mesopore system with pore volume of up to 0.44 cm$^3$/g. Compared to existing carbon templating methods, this method does not rely on the availability of special and expensive chemicals, only on the mesoporous silica that are used widely and can be obtained easily by precipitation. Moreover, we show that the use of novel synthesis procedure based on the carbon templating method with an in-situ-generated carbon template allowed us to obtain mesoporous zeolite Beta single crystal materials.

Fig. 5. TEM images of mesoporous Beta-type materials.

4. Conclusions

In conclusion, the preparation of mesoporous ZSM-11, Beta and Y-type zeolite single crystals modified with Ni-nanoparticles based on the carbon templating method with an in-situ-generated carbon template is reported for the first time. The obtained zeolite materials combine high crystallinity with an intracrystalline mesopore system with pore volume of up to 0.44 cm$^3$/g. Compared to existing carbon templating procedures, this method does not rely on the availability of special and expensive chemicals, only on the mesoporous silica that are used widely and can be obtained easily by precipitation. Moreover, we show that the use of novel synthesis procedure based on the carbon templating method with an in-situ-generated carbon template allowed us to obtain mesoporous zeolite Beta single crystal materials. TEM images of the mesoporous Ni-ZSM-11 zeolite are presented in the supplementary material.

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Notes and references


