Mordenite nanorods prepared by an inexpensive pyrrolidine-based mesoporogen for alkane hydroisomerization

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Mordenite Nanorods Prepared by an Inexpensive Pyrrolidine-based Mesoporogen for Alkane Hydroisomerization


We report the synthesis of hierarchical mordenite zeolite nanorods in one step using inexpensive mono-quaternary ammonium N-cetyl-N-methylpyrrolidinium (C$_{16}$NMP) as mesoporogen to the synthesis gel. The presence of a small amount of C$_{16}$NMP results in the formation of 0.6–1 μm rods-like crystals oriented along the c-axis with a high mesoporous volume (0.12 cm$^3$·g$^{-1}$) and external surface area (~90 m$^2$·g$^{-1}$) compared to bulk mordenite. Acidity characterization shows that the presence of C$_{16}$NMP during mordenite formation leads to a redistribution of aluminum in the zeolite framework: the amount of Brønsted acid sites in the side-pockets (8MR main channels) is increased at the expense of those in the 12MR main channels. As these latter acid sites are the ones involved in the conversion of alkenes intermediates in bifunctional hydroconversion of alkanes, an optimized hierarchical mordenite prepared with C$_{16}$NMP displays a more ideal hydrocracking selectivity than bulk MOR prepared solely with sodium.

Introduction

Zeolites are crystalline microporous aluminosilicates with widely varying topologies giving rise to more than 200 different framework types that have already been synthesized.[1] Their high surface area, high thermal stability, uniform micropore structure and tunable surface acidity contribute to their widespread application in industry as ion-exchangers, molecular sieves, adsorbents and foremost catalysts.[2] Only a limited number of zeolites are used in practice. Among them, mordenite is extensively used as a catalyst for hydrocarbon conversion, i.e. (hydro)isomerization,[3] alkylation,[4] hydrocracking and dewaxing,[5] as well as in the synthesis of substituted amines.[6]

Mordenite (MOR) zeolite contains primary parallel channels of 12-membered ring (6.5×7.0 Å) and 8-membered ring (2.6×5.7 Å) size along the c-axis, which are connected via tortuous side pockets with an aperture of 3.4×4.8 Å in the b-direction[7,8] (Figure 1). The unidimensional (“tubular”) pores impose diffusion limitations, which may hinder the transport of reactant and product molecules from approaching and leaving the active sites inside the pores. This can result in a decreased utilization of the microporous space and prompt coke deposition.[9] The introduction of a second level of intracrystalline porosity to the MOR pore system would be advantageous to the many acid-catalyzed hydrocarbon conversion reactions that involve large paraffinic and aromatic molecules. A general “top-down” approach to prepare mesoporous mordenite zeolites via desilication,[4,10,11] dealumination[12–15] or a combination of these approaches[16–19] has been extensively examined. Even though these techniques are commercially available and can be scaled up, there is little control over the textural and acidic properties of the final materials. Several groups applied a recrystallisation strategy where desilication occurs in the presence of organic surfactants such as cetyltrimethylammonium bromide[20] or tetrabutylammonium hydroxide.[21] While the degree of recrystallization is enhanced, formation of less active impurity phases such as MCM-41 also takes place.[22] A direct synthesis in the presence of mesoporous structure directing agents (SDA) molecules provides a possibility to overcome issues mentioned

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Figure 1. Mordenite zeolite structure.
above.\textsuperscript{[22–24]} These soft templating procedures offer the opportunity to tune the mesopore system.\textsuperscript{[25]}

The soft-templating approaches already known for the synthesis of hierarchical MOR zeolite are summarized in Table S1. Generally, organosilanes and mono- or multi-quater-
nary ammonium salts have been employed to introduce mesoporosity in MOR zeolite. Nearly all of the described recipes involve the addition of a mesoporegen to a synthesis mixture which contains seeds\textsuperscript{[25–28]} of conventional SDA\textsubscript{\textsuperscript{\textsuperscript{35,36}}} or require complex cationic surfactants with two or more ammonium ions\textsuperscript{[29,31–34]} There are only few reports that claim the formation of hierarchical MOR zeolite with a mono-quaternary ammonium surfactant or aniline as a single SDA.\textsuperscript{[25]}

The synthesis mesoporous MOR can also be achieved in a template-free synthesis under relatively harsh conditions (T \( \geq \) 170 °C).\textsuperscript{[6,37,38]}

In this work, we synthesized hierarchical MOR with a nanorod-shaped morphology in a single step using N-cetyl-N-
methylpyrrolidinium bromide. This organic template contains a bulky and polar mono-quaternary ammonium N-methylpyrrolidi-
dine head group and an alkyl (C\textsubscript{16}) chain as the hydrophobic tail. The synthesis procedure was optimized with respect to the mesoporegen concentration and the obtained zeolite samples were characterized for their textural and acidic properties. The catalytic performance of Pd-loaded mesoporous MOR catalyst in n-hexadecane hydrosolvolysis in comparison to a conven-
tional bulk MOR zeolite was used to evaluate the benefit of hierarchical structuring of MOR.

**Results and Discussion**

We employed a synthesis approach to obtain MOR zeolite that does not use an organic template. The precursor solution is obtained by mixing together faujasite (FAU) zeolite and sodium silicate as aluminum and silicon sources. Starting from a gel with a composition 2.47 Na:\textsubscript{2}O:0.33 Al\textsubscript{2}O\textsubscript{3}:10 SiO\textsubscript{2}:256 H\textsubscript{2}O, we obtained a highly crystalline MOR zeolite (MOR–C, Figure 2) after 6 days of hydrothermal synthesis at 140 °C. Mesoporous zeolites were prepared by adding C\textsubscript{16}NMP (SDA/SiO\textsubscript{2} = 0.015–0.04) to a similar synthesis gel. In most cases, pure crystalline MOR zeolite was obtained. Only at higher SDA concentration (SDA/SiO\textsubscript{2} = 0.035–0.04), the solid product contained a small amount of FAU (Figure 2a). As compared to reference MOR–C, the diffraction lines of h\(\text{k}\)0 reflections of the C\textsubscript{16}NMP-templated MOR zeolites were broadened, which can be attributed to a decreased size of the crystalline domains in \(ab\)-directions.\textsuperscript{[26]}

From the intensity of the h00 and 0\(\text{k}\)0 reflections, we can obtain information about the crystal orientation. The intensity of the diffraction line at \(2\theta = 9.75\) degrees belonging to the [200] reflection is strongly decreased (Figure 2b) compared to MOR–C, while the intensity of the [020] reflection at \(2\theta = 8.61\) degrees is less substantially affected. These differences show that the crystal size is more strongly reduced in the \(ab\)-direction than in the \(c\)-direction. This effect is most pronounced for the MOR-0.25 sample.

SEM images of the MOR zeolites prepared at low SDA/SiO\textsubscript{2} ratio (Figure 3a–c) show a rod-like morphology with crystals with a length of 0.6-1 m, organized into larger dense-packed particles. The crystal sizes increase when more C\textsubscript{16}NMP is added to the synthesis gel (Figure 3d–f). Without an organic SDA, the MOR crystals have the typical prismatic shape (Figure S5).\textsuperscript{[19]}

The Ar physisorption isotherm for conventional MOR–C has the type I shape typical of microporous materials. The samples synthesized with C\textsubscript{16}NMP as SDA have a type IV isotherm, pointing to the additional presence of mesopores (Figure 4). The microporous volumes of the hierarchical zeolites are comparable to the microporous volume of the bulk counterpart (=0.11 cm\textsuperscript{3}g\textsuperscript{-1}). This is in keeping with the high crystallinity derived from XRD analysis. The largest mesoporous volume of 0.12 cm\textsuperscript{3}g\textsuperscript{-1} and the largest external surface area of 88.5 m\textsuperscript{2}g\textsuperscript{-1} are for the sample prepared with a SDA/SiO\textsubscript{2} ratio of 0.025 (Table S2). A further increase of the SDA content led to a slightly lower mesoporous volume, likely due to the larger size of the crystals. Pore size distributions derived from the
desorption-branch of the isotherm using the BJH-method show relatively uniform mesopores of about 3.75 nm for all hierarchical materials (Figure 4b). At this stage, we decided to focus on MOR-0.25 as this sample combines optimal textural properties with high crystallinity and phase purity.

Elemental analysis of optimized MOR-0.25 sample showed a Si/Al ratio of 9.5 (Si/Al 15 in the initial synthesis gel). To determine whether it is possible to synthesize a mesoporous MOR with lower Al content, we carried out a hydrothermal synthesis with an initial Si/Al ratio of 25. Although a pure MOR phase was obtained (Figure S6), the morphology of the material was very irregular, consisting of an agglomeration of non-uniform crystals (Figure S7). This sample only had a modest mesoporous volume of 0.04 cm$^3$g$^{-1}$ (Figure S8). We also evaluated whether Al(OH)$_3$ could serve as an aluminum source. While the morphology of the resulting crystals was the same as in the synthesis with FAU, larger particles (>2 μm) with a lower Si/Al ratio of 7.2 were obtained (Figure S9 and S10).

TEM analysis showed that the MOR-0.25 sample (Figure 5b) consists of well-defined stacks of nanorods with a width of about 30 nm. From inspection of the d-spacings, we find that the nanorods are oriented parallel to the c-axis, i.e. the 1.33 nm...
and 0.90 nm lattice distances visible in Figure 6 and attributed to the [110] and [200] planes, respectively.

Such rod-like structures are likely formed because of the hydrophilic head group is located inside the micropores, for instance in the side-pockets or at the entrance of the side pockets, while the long hydrophobic tail is blocking crystal growth, resulting a smaller domain size in the ab-dimensions.

This would constitute a similar growth mechanism as observed for nanosheets of ZSM-5 zeolite. On the contrary, the MOR–C sample consists of micrometer-sized crystals with 0.8-2 μm particle length (Figure 5a, Figure S5).

To evaluate the acidic properties of obtained MOR samples, the nature of the hydroxyl groups was investigated by IR spectroscopy (Figure 7). Several vibrational bands were identi-
fied in the \( \nu_{\text{OH}} \) region: bridging hydroxyl groups at 3606 cm\(^{-1}\), external and internal silanols at 3745 cm\(^{-1}\) and 3733 cm\(^{-1}\), respectively.\(^{[40]}\) The band at 3657 cm\(^{-1}\) can be assigned to OH groups connected to extraframework aluminum (EFAL) or Al-OH groups partially bounded to the zeolite lattice.\(^{[41]}\)

MOR zeolite contains various types of Brønsted acid sites (BAS), which can be distinguished on the basis of the IR frequency of the hydroxyl groups.\(^{[42–45]}\) Lukyanov et al. developed a three-band curve fitting procedure involving the deconvolution of the main bridging hydroxyl band.\(^{[42,45]}\) The three types of acid sites (Figure 8) are (i) BAS located in the 8-membered ring (8MR) side-pockets of MOR, giving rise to a low-frequency (LF) band at 3587 cm\(^{-1}\), (ii) BAS at the interface between 8MR and 12MR pores, resulting in a high-frequency (HF) band at 3606 cm\(^{-1}\) and (iii) BAS in the main 12MR channels, leading to a top-frequency (TF) band at 3619 cm\(^{-1}\).

Following this approach, we deconvoluted the hydroxyl region of the IR spectra and found considerable difference in the population of discrete BAS between MOR–C and MOR-0.25 (Figure 9). The total amount of acid sites in MOR-0.25 sample is 25% lower than that in MOR–C, which is consistent with the lower Al content of MOR-0.25 (Table S3) and the slightly larger amount of EFAL (Figure 9a–b). Figure 9c shows that the fraction of BAS located in 8MR side-pockets is higher for MOR-0.25 (47%) than for MOR–C (31%). At the same time, we detected a substantial reduction in BAS situated in the channel interfaces, whereas the number of acid sites in the main channels remained similar. This change in the Al distribution over the zeolite framework is most likely due to the presence of the charged C\(_6\)NMP during hydrothermal synthesis. We speculate that the head group of the mesoporogen is located close to the Al in the side pockets, whereas other Al species placed in the large 12MR channels and/or the interface between 8MR and 12MR channels are instead stabilized by Na\(^+\) cation. This finding is supported by IR spectra of adsorbed pyridine (Figure S11). We observed a decrease in the total amount of HF and TF types of BAS, which are most likely available for bulk pyridine molecule after the introduction of mesoporosity into MOR zeolite (Table S4).

The \(^{27}\)Al MAS NMR spectra of the MOR samples in the proton form feature mainly a signal of tetrahedrally coordinated Al species (\(\geq 75\%\)) (Figure 10). The spectra also show a broad peak at \(\sim 0\) ppm, which can be attributed to EFAL species.\(^{[46]}\) Such a relatively large amount of EFAL species is usually observed for bulk MOR\(^{[18]}\) as well as nanostructured MOR zeolites.\(^{[35,38]}\) The broadening of the main signal is related to a different environment of Al\(^{IV}\) and not the presence of penta-coordinated aluminum because a characteristic signal for such species (centered at \(\sim 30\) ppm) is absent.\(^{[47,48]}\)

The different zeolites were compared for their catalytic activity in the hydroconversion of n-hexadecane. N-hexadecane conversion for the different MOR samples is presented as a function of the temperature in Figure 11. The zeolites were loaded with enough Pd to ensure a sufficient hydrogenation activity (enough metal nPd in comparison to acid nH\(^+\) sites) for intermediate olefin
conversion reactions to be limiting the overall conversion rate. MOR-C and MOR-0.25 displayed similar apparent activation energies of 138 kJ/mol and 135 kJ/mol, respectively (Figure 12). The Pd metal dispersion was estimated by H\textsubscript{2} chemisorption and the acid site density by IR spectroscopy of adsorbed pyridine (Table S4). As the Pd dispersion in the reduced Pd/H-MOR catalysts is comparable, activity differences must be due to the changes in the concentration and/or the location of the BAS. The product distributions, which are also plotted in Figure 11, are strongly affected by the texture of the support. The MOR–C zeolite exhibits a high selectivity to cracked products, even at a low n-hexadecane conversion. The skewed cracked product distribution for this sample (Figure 11b) is indicative of secondary cracking, associated with a long residence time of olefinic intermediates in the zeolite domains. On the contrary, the MOR-0.25 sample exhibits a much higher selectivity to isomerization products at low conversion (<10%) with a more symmetric distribution of cracked products, close to the pattern expected for ideal hydrocracking.

Taking into account that acid sites located in the 8MR side-pockets are not accessible to alkanes,\textsuperscript{31,32,33} the improved catalytic behavior of MOR-0.25 can be explained by a decreased amount of BAS in the main 12MR channels, where the hydroconversion reaction of alkenes takes place. The lower accessible acidity of Pd/MOR-0.25 shifts the hydrogenation/acidity balance towards ideal hydrocracking behavior. This is in line with the results of a study of the hydroisomerization of n-pentane in which the Si/Al ratio for the Pt/MOR catalyst was varied.\textsuperscript{34} An additional explanation can be the reduced zeolite domain size, which decreases the residence time of the reaction intermediates in the zeolite and, therefore, cracking. To fully understand whether reduced acidity or mesoporosity dominates the improvement of catalytic performance, a more relevant reference sample is required. Yet, preparation such a catalyst from parent mordenite, synthesized with a typical Si/Al ratio around 7 by dealumination would modify its textural and acidic properties simultaneously. We note that, despite the improved behavior due to the lowered acidity, the total cracking selectivity of MOR-0.25 is still relatively high, when the aim is to achieve isomerization, for instance, for the reduction of the cloud point of diesel. Therefore, further strategies need to be developed to lower the framework Al density of these improved hierarchical MOR zeolites.

**Conclusions**

We achieved the direct synthesis of hierarchical c-axis oriented MOR nanorods in the presence of an inexpensive C\textsubscript{16}NMP mesoporegen. Characterization shows that the use of the mesoporegen in addition the sodium as an inorganic template results in a reduction of the crystal growth in the ab-directions and redistribution of Al in the framework. Specifically, the use of C\textsubscript{16}NMP results in an increase of the amount of BAS in the side-pockets (8MR channels) of MOR at the expense of the BAS in 12MR. As these latter BAS are the ones involved in the conversion of alkene intermediates in the bifunctional hydroconversion of alkanes, an optimized hierarchical MOR prepared with C\textsubscript{16}NMP displays a more ideal hydrocracking selectivity than bulk MOR prepared solely with sodium as a template.
Experimental Section

Preparation of N,N-methylhexadecylpyrrolidinium Bromide (C_{16}\text{NMP})

0.013 mol of 1-bromohexadecane (Sigma Aldrich, 98.0 %) and 0.016 mol N-methylpyrrolidine (Sigma Aldrich, 98.0 %) were dissolved in 50 ml ethanol (Biosolve, 99.9 %) and heated at 70 °C for 20 h under nitrogen atmosphere. After evaporation of ethanol and addition of the diethyl ether (Biosolve, 99.5 %), a white powder precipitated. This solid product was filtered and dried in a vacuum oven at 50 °C for 12 h. The purity of the organic surfactant C_{16}H_{33}+[-methylpyrrolidine] was analyzed by $^1$H and $^{13}$C NMR after dissolution in CDCl$_3$. The product yield was 87 %.

Preparation of MOR Zeolite

C_{16}H_{33}+[-methylpyrrolidine] was used in the synthesis of MOR zeolite. We were inspired by the work of Ryoo and coworkers, where MOR nanocrystals were obtained in the presence of a multivalent surfactant as an solitary capping agent. In the current work, the bromide form of C_{16}NMP was dissolved in deionized water at room temperature. Subsequently, a sodium silicate solution (Merck, SiO$_2$, 27.0 %, Na$_2$O 8.0 %) was added dropwise to this solution and stirred for 15 min. Then, NH$_4$Y zeolite (Alfa Aesar,
Calcined zeolites samples were subsequently ion-exchanged three times with 1.0 M NH₃ suspensions in ethanol and dispersed over a carbon-coated holey Cu₃NMP (MOR–C).

Characterizations

Basic characterization. The crystallinity of the zeolite samples was evaluated by recording X-Ray Diffraction (XRD) patterns on a Bruker D² Endeavor powder diffraction system. Cu Kα radiation was used in the 2θ range of 5–60° with a step size 0.02° and the time per step of 0.4 s. Textural properties were determined by Ar physisorption at −186 °C on a Micromeritics ASAP-2020 instrument. The zeolite powders were outgassed at 400 °C and a residual pressure of 5 pbar pressure for 8 h prior measurement. The microporous volume was calculated by the t-plot method using a thickness range from 3.5 Å to 7.5 Å. The total pore volume was measured at P/P₀ = 0.95. The elemental composition of MOR zeolites was determined by ICP-OES (inductively coupled plasma optical emission spectroscopy) by a Spectro CIROS CCD ICP spectrometer with axial plasma viewing. For this purpose, the samples were dissolved in an 1:1:1 (by weight) mixture of HF (40%):HNO₃:HO (x:0.15, 0.20, 0.25, 0.30, 0.35, 0.40). A conventional bulk mordenite sample was prepared without addition of C₃H₇NMP (MOR–C).

Electron microscopy. Transmission electron microscopy (TEM) pictures were taken on a FEI Tecnai 20 at 200 kV. The samples were suspended in ethanol and dispersed over a carbon-coated holey Cu grid. Scanning electron microscopy (SEM) images were taken by a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 3 kV and spot size 4.5.

IR spectroscopy. IR spectra of the zeolites were recorded in the range of 4000–400 cm⁻¹ on a Bruker Vertex 70v FTIR spectrometer. The spectra were acquired at a 2 cm⁻¹ resolution and were obtained by averaging 64 individual scans. The samples were prepared as thin wafers of ca. 12 mg. The wafer with a diameter of 13 mm was placed inside a controlled-environment transmission IR cell. The samples were activated at 550 °C in air flow during 3 h and after cooling the cell to 150 °C, the spectra were measured under vacuum. Pyridine was introduced into the IR cell from an ampoule kept at room temperature. After exposure to pyridine for 10 min, the sample was evacuated over three consecutive 1 h periods at 150 °C, 300 °C and 500 °C. Each spectrum was recorded after cooling the cell to 150 °C. The spectra were normalized by the weight of the wafer.

NMR spectroscopy. Magic-angle spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were recorded at room temperature with 11.7 Tesla Bruker DMX500 NMR spectrometer. ²⁷Al MAS NMR spectra were recorded at 132 MHz with a spinning rate of 25 kHz and a single excitation pulse length of 1 μs with a 1 s repetition time. The ²⁷Al chemical shift was referenced to the signal of a saturated solution of Al(NO₃)₃.

H₂ Chemisorption. H₂ uptake measurements were used to titrate the surface metal atoms and to provide an estimate of the active sites on the catalysts. Usually, 50 mg of the sample was loaded in a quartz reactor. Prior to dosing, samples were reduced in flowing H₂ (1 h, 400 °C, 3 °C/min), evacuated at 450 °C for 1 h to remove chemisorbed hydrogen and cooled to 80 °C under vacuum. Analysis was then performed at 80 °C by collecting an adsorption isotherm to determine the H₂ uptakes.

Catalytic Activity Measurements

In order to determine the catalytic performance of the Pd-loaded zeolites in n-hexadecane (n-C₁₆) hydroconversion, the catalyst was dried in the reactor for 1 h in a He flow at 200 °C (atmospheric pressure) followed by reduction in a pure H₂ flow at 60 bar. During reduction, the temperature was increased from 100 °C to 400 °C at a rate of 3 °C/min to 400 °C followed by an isothermal period of 1 h. Then, the temperature of the catalyst bed was lowered to 200 °C and the packed bed was wetted by the n-C₁₆ feed, maintaining a liquid flow rate of 1 ml/min for 10 min. The reactor was operated at a H₂/n-C₁₆ molar ratio of 20 and a weight hourly space velocity (WHSV) of 10 gC₆H₁₃ mol g⁻¹ h⁻¹. The reaction temperature was increased stepwise and the reaction was equilibrated for 3 h before product sampling. The reactor effluent was analyzed by a gas chromatograph, which was equipped with an RTX-1 column and a flame ionization detector.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: hierarchical zeolite • mordenite • nanorods • paraffin hydroconversion