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Hierarchically Porous (Alumino)Silicates Prepared by an Imidazole-Based Surfactant and Their Application in Acid-Catalyzed Reactions

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 Supporting Information

ABSTRACT: In this work, we developed a novel strategy to synthesize porous (alumino)silicate materials using a single structure-directing agent composed of an imidazolium surfactant. These materials can be synthesized with a very high surface area (>800 m² g⁻¹), and their surface properties can be tuned to favor catalytic performance, where the shape selective nature of the microporous and mesoporous is often beneficial.

1. INTRODUCTION

Porous silicas and their aluminum-containing analogues are widely used in many technological settings mainly in adsorption and catalysis but also in drug delivery and other biomedical applications. These materials can be synthesized with a very high surface area (>800 m² g⁻¹), and their surface properties can be tuned to favor catalytic performance, where the shape selective nature of the microporous and mesoporous is often beneficial.

One of the most important contributions to the field of porous silicas was the discovery of MCM-41, an ordered mesoporous silicas in which cylindrical pores are organized in hexagonal arrays. MCM-41 can be synthesized by condensation of silica around organic micelles, formed by a cationic surfactants, e.g., cetyltrimethylammonium bromide (CTAB), in a basic aqueous medium. Changing the length of the hydrophobic carbon tail of the surfactant allows tuning the degree of silica condensation and tune the textural and morphological properties of the final materials. By varying the aluminum concentration in the gel, we can obtain mesoporous amorphous silica–alumina or crystalline mordenite zeolite with, respectively, weak and strong Brønsted acid sites. Obtained acidic silica–alumina materials displayed promising performance in catalytic reactions of linear paraffin hydroisomerization and Friedel–Crafts alkylation of benzene with benzyl alcohol.

KEYWORDS: surfactant, imidazole, mesoporous silica, hierarchical mordenite, catalysis

mesoporous silicas, the zeolite structure is usually formed by the condensation of silica around small organic or inorganic cations that act as structure-directing agents (SDA). The microporous channels (typically smaller than 1 nm) can impose severe intracrystalline diffusion limitations which can be overcome by introducing a secondary level of mesoporosity. For this purpose, many techniques have been developed including bottom-up and top-down approaches.

One particularly interesting approach to introduce this additional porosity is to use a single cationic surfactant, e.g., mono- or diquaternary ammonium salts, to direct at the same time the growth of the microporous network and to generate the mesopores/voids within the zeolite crystal. There are only a few examples of such successful direct single-template synthesis of mesoporous zeolite. Complex quaternary ammonium salts have been employed to obtain several topologies, e.g., FAU, MOR, and MFI zeolites. On the other hand, the use of a simple surfactant (e.g., cetyltrimethylammonium hydroxide (CTAOH)) usually results only in the formation of silicalite or ZSM-5. We recently demonstrated that an inexpensive mono-quaternary ammonium salt, containing a cyclic N-methylpyrrolidinium head group, can be an efficient surfactant for the direct synthesis of hierarchically porous mordenite (MOR) zeolite.

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In this work, we developed a novel strategy to obtain several ordered mesoporous materials using 1,2-dimethyl-3-hexadecyl-1H-imidazol-3-ium bromide (C_{16}dMImz) as an organic SDA. Amorphous layered silica with a high surface area (1200 m^2 g^{-1}) was obtained in the absence of aluminum. Addition of a small amount of Al resulted in a layered silica—alumina (800 m^2 g^{-1}) with weak acidity, while at higher Al content a highly crystalline hierarchically porous MOR zeolite (V_{meso} 0.08 cm^3 g^{-1}) was obtained. The synthesis procedure was optimized with respect to the aluminum concentration and temperature, and the obtained materials were characterized in detail for their chemical, textual, and acidic properties. The obtained amorphous silica—alumina with weak Bronsted acidity displayed a promising catalytic performance in the n-hexadecane hydroisomerization reaction. Moreover, strongly Bronsted acidic mordenite nanorods were found to be efficient for the Friedel–Crafts alkylation of benzene with benzyl alcohol.

2. EXPERIMENTAL SECTION

2.1. Preparation of SDA. 2.1.1. 1,2-Dimethyl-3-hexadecyl-1H-imidazol-3-ium Bromide (C_{16}dMImz). In total, 0.013 mol of 1-bromohexadecane (Sigma-Aldrich, 98.0%) and 0.016 mol of 1,2-dimethylimidazolide (Sigma-Aldrich, 97.0%) were dissolved in a 50 mL mixture of ethanol (Biosolve, 99.9%) and acetonitrile (Biosolve, 99.9%) (1:5 molar ratio) and heated at 70 °C for 16 h under nitrogen atmosphere. After evaporation of the solvents and addition of diethyl ether (Biosolve, 99.5%), a white powder precipitated out of solution. 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}+[1,2-dimethyl-3-imidazolium] was analyzed by H, ^{13}C, gHSQC, and gCOSY NMR after dissolution in CDCl3 (Figures S1–S4). The product yield was 75%.

2.2. Synthesis of Materials. First, the bromide form of C_{16}dMImz was dissolved in deionized water at room temperature. To synthesize aluminum-free silica, sodium silicate (Merck, SiO_{2} 27.0%, Na₂O 8.0%) was used. We added the silica source dropwise to the template solution while stirring. Aluminum-containing silica was obtained by adding Al(OH)₃ (Sigma-Aldrich, 99.8% reagent grade) to the template solution under continuous stirring. The molar composition of the synthesis gel was 0.2 C_{16}dMImz/2.70 Na₂O/x Al₂O₃/10 SiO₂/300 H₂O (x = 0.0–0.5). After vigorous stirring for 2 h at ambient temperature, the resulting gel was transferred into a Teflon-lined stainless-steel autoclave and heated at temperatures in the 105–186 °C range for 24–144 h under rotation (50 rpm). The resulting solid product was filtered, thoroughly washed with deionized water, and dried in air at 110 °C before calcination in air at 550 °C for 6 h. Amorphous products were denoted according to the established morphology: ordered mesoporous silica, OMS; layered silica, LS; layered silica-alumina, Al-LS. Depending on the Si/Al ratio of the synthesis gel, as-synthesized mesoporous zeolites were denoted as mMOR-10 and mMOR-15. Conventional bulk mordenite reference samples were also prepared without addition of C_{16}dMImz and denoted as MOR-10 and MOR-15.

2.3. Catalyst Preparation. Al-containing samples were converted to their protonated form by ion exchange, which was performed in three consecutive steps with an aqueous 1.0 M NH₄NO₃ solution (1 g of the solid per 100 mL of the solution, 3 h, 70 °C). Then, the ammonium form of the product was separated from the solution via centrifugation followed by drying at 110 °C and calcination at 500 °C for 4 h (heating rate of 0.5 °C/min) to obtain the final proton form. The proton forms of the amorphous silica-alumina samples were then loaded with 1 wt % Pd by incipient wetness impregnation using an aqueous Pd(NO₃)₂ solution of appropriate concentration. The resulting catalysts were calcined in air at 450 °C under flowing air for 4 h.

2.4. Characterization. 2.4.1. Basic Characterization. The crystallinity and phase purity of all samples was determined by X-ray diffraction (XRD) with a Bruker D2 Phaser powder diffractometer with Cu Kα radiation. XRD patterns were obtained in the 2θ range of 5–60°, with a step size of 0.02°. Small-angle XRD patterns were recorded in the 2θ range of 0.7–7° with a step size of 0.004°.

Textural properties of the samples were investigated using Ar physisorption. Adsorption and desorption isotherms were recorded at −186 °C on a Micrometrics ASAP-2020 apparatus. Prior to measurement, the samples were outgassed at 400 °C to a residual pressure of 5 μbar for 8 h. The microporous volume was calculated by the t-plot and NLDFT methods using the 3.5–8.0 Å thickness range. The mesoporous volume was determined from the adsorption branch of the isotherms by the Barrett–Joyner–Halenda (BJH) method. The pore size distribution was derived using the NLDFT method. The total pore volume was recorded at P/P₀ = 0.95.

The elemental composition of aluminum-containing products was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Spectro CIROS CCD ICP spectrometer with axial plasma viewing. For these measurements, the samples were dissolved in a 1:1:1 (by weight) mixture of HF (40%)/HNO₃ (60%)/H₂O.

2.4.2. Electron Microscopy. Scanning electron microscopy (SEM) images were obtained using a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 3 kV and a spot size of 4.5. Transmission electron microscopy (TEM) images were recorded on a Tecnai 20 (type Sphere, FEI, now Thermo Fischer Scientific) operated at 200 kV. TEM sample preparation involved sonication of the samples in pure ethanol (Biosolve, extra dry, 99.9%) and applying a few droplets of the suspension to a 200 mesh Cu TEM grid with a holey carbon support film.

2.4.3. FTIR Spectroscopy. All IR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer in the range of 4000–400 cm⁻¹. The spectra were recorded at a 2 cm⁻¹ resolution and as an average of 64 scans. The samples were prepared as thin wafers of ~10–12 mg with a diameter of 13 mm and placed inside a controlled-environment transmission IR cell. The samples were then activated at 550 °C in air flow for 3 h before cooling the cell to 150 °C and measuring the spectra under vacuum. Pyridine was then introduced into the IR cell from an ampule kept at room temperature. After exposure for 10 min to pyridine, the sample was evacuated over three consecutive 1 h periods at 150 °C, 300 °C, and 500 °C, with a spectrum taken after each hour and cooled to 150 °C. All spectra were normalized by the weight of the wafer.

2.4.4. NMR Spectroscopy. Magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded at room temperature with a 11.7 Tesla Bruker DMSX500 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 reference signal for the ²⁷Al chemical shift was a saturated solution of Al(NO₃)₃.

2.4.5. Thermogravimetric Analysis (TGA). TGA analysis was performed on a Mettler Toledo TGA/DSC 1 instrument. About 10 mg of the sample was placed in an alumina crucible. The uncovered crucible was heated to 750 °C at a rate 5 °C/min in 40 mL/min He and 20 mL/min O₂ flow.

2.4.6. H₂ Chemisorption. H₂ uptake measurements were used to titrate the surface metal atoms and to provide an estimate of the number of active sites on the catalyst. A total of 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 uptake.

2.5. Catalytic Activity Measurements. 2.5.1. Hydroconversion of n-Hexadecane. To determine the catalytic performance of Pd-loaded silica-alumina in n-hexadecane (n-C₁₆), hydroconversion, the catalyst was pretreated in a He flow at 200 °C under atmospheric pressure for 1 h followed by reduction in a pure H₂ flow at 60 bar. During reduction, the temperature was increased from 100 to 400 °C at a rate of 3 °C/min to 400 °C followed by an isothermal period of 1 h. The temperature of the catalyst bed was then lowered to 200 °C, and the packed bed wetted by the n-C₁₆, 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 g_{n-C16} g_{cat}^{-1} h^{-1}. The reaction temperature was increased stepwise and the reaction 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.

2.5.2. Friedel–Crafts Alkylation Reaction of Benzene with Benzyl Alcohol. The liquid phase Friedel–Crafts alkylation reaction of benzene (B) with benzyl alcohol (BA) was carried out in a glass flask equipped with a PTFE septum. The reaction took place under atmospheric pressure and magnetic stirring at 900 rpm. The flask was placed in a temperature-controlled oil bath. Before reaction, 0.1 g of catalyst (activated at 500 °C in air for 4 h) was mixed with benzene (25.7 mL) in an Ar glovebox. After reaching the reaction temperature of 80 °C and depressurizing the reactor through a side vessel, the reaction was maintained for 30 min. Then, 0.6 mL of BA was added and this action was taken as the start of the reaction. Reaction mixture aliquots of 150 μL were taken at regular time intervals during the reaction and were separated from the zeolite catalyst by filtration. The samples were further analyzed by a gas chromatograph (GC, Shimadzu GC-17A) equipped with a flame ionization detector (FID) and an Rxi-5 ms capillary column (30-m long, 0.25 mm i.d., and 0.5 μm thickness).

3. RESULTS AND DISCUSSION

In this work, we employed an approach, where only one cationic surfactant (C16dMImz) was used for the synthesis of different (alumina)silicate products, ranging from amorphous mesoporous silica to hierarchically porous crystalline zeolite. The overall strategy and the types of prepared materials are shown in Scheme 1.

**Scheme 1. Strategy in the Synthesis of Porous Silica (Alumina) and Zeolite Materials**

An ordered mesoporous silica with hexagonal pore structure was formed after 1 day of hydrothermal synthesis at 105 °C in the presence of C16dMImz (Figure 1). Prolonging the synthesis time to 6 days led to the shift of the XRD peak belonging to the [100] reflection of the hexagonal structure to a lower angle (from 2θ = 2.77° to 2θ = 2.72°). This can be related to a slight increase in the pore size. Additionally, after extending the synthesis time, the [100] peak became less symmetric, and the [200] reflection at 2θ = 5.42° almost disappeared after 6 days of synthesis, indicating some structural disordering. The d-spacings (d_{100}) were calculated using Bragg’s law after 1 and 6 days synthesis to be 32.0 and 32.5 Å, respectively. The obtained products were denoted as OMS (ordered mesoporous silica).

The Ar physisorption isotherms of the samples are of the type IV shape, typical for mesoporous materials (Figure 2a).26 The calcined products are characterized by a large total pore volume (~0.76 cm³ g⁻¹) and BET surface area (~1100 m² g⁻¹) (Table S1). In the line with XRD, these values are slightly lower after 6 days than after 1 day synthesis. The pore size distributions show relatively uniform mesopores of about 2.9 nm for both products with comparable (~0.80 nm) wall thickness (Figure 2b and Table S1).

TEM analysis of the OMS-1d and OMS-6d samples revealed a hexagonal array of pores (Figure 3b). The pore sizes are in a narrow range from 2.8 to 3.1 nm determined by inspection of several TEM images and supported by XRD and Ar physisorption data. In turn, SEM images revealed the different morphologies of the samples at different synthesis times (Figure 3c, d). Agglomerations without a specific shape with a smooth outer surface were detected for the 1-day sample, while longer synthesis time leads to the formation of a more “jagged” phase.

3.2. Layered Silica. The Ar physisorption, XRD, and SEM results revealed a possible transition of the initially formed ordered mesoporous silica to a denser phase, the formation of which was driven by a longer synthesis. Such phase transformations of MCM-41/MCM-48 to semi-crystalline layered silica during hydrothermal synthesis have been reported before.10,27,28 Typically, high temperature (135–150 °C) and/or longer synthesis (>5 days) are required for this transformation. Therefore, we investigated the influence of synthesis temperature (115–170 °C) on the structural changes of the OMS materials.

**Figure 1.** (a) Small and (b) wide angle XRD patterns of calcined mesoporous silica at different synthesis times at 105 °C.
Figure 2. (a) Ar physisorption isotherms and (b) pore size distribution of calcined OMS samples after different hydrothermal synthesis times at 105 °C. The pore size distributions were calculated via the NLDFT approach and vertically offset by equal intervals of 0.003 cm$^3$ g$^{-1}$ nm$^{-1}$.

Figure 3. TEM and SEM images of as-synthesized mesoporous silicas after (a,c) 1 day and (b,d) 6 days of hydrothermal synthesis at 105 °C.

Figure 4. (a) Small and (b) wide angle XRD patterns of calcined silica materials obtained after 6 days of hydrothermal crystallization at different temperatures.
XRD of the obtained materials pointed to a structural evolution from amorphous silica with a hexagonal structure at 105 °C (Figure 1a), via several layered silica intermediates with a different degree of crystallinity at 115–160 °C for 6 days (Figure 4), to a crystalline α-quartz phase at 170 °C after 13 days (Figure S5). The obtained layered silica (LS) at 115–140 °C are characterized by single diffraction peak at 2θ = 2.28° (d100 = 38.53 Å) at a small angle (Figure 4a) and the presence of some short-range order, confirmed by a broad diffraction feature at 2θ ∼ 13.0° (Figure 4b). The increase in temperature to 160 °C resulted in a more ordered material. The LS (160 °C) material has a similar XRD pattern as magadiite silicate (reflections at 2θ ∼ 5.2°, 10.4°, 26.0°, and 49.4°). A further increase in temperature led to the development of sharp diffraction lines of α-quartz, with some magadiite phase still being present (Figure 4b).

Clearly, with increasing temperature, the influence of C16dMImz on the structure of the final silica material diminishes. This observation is also confirmed by the gradual decrease in the amount of SDA occluded in the pores with increasing synthesis temperature (Figure S6). At high temperature, the formation of layered silicates such as magadiite and α-quartz can occur without addition of organic molecules in a thermodynamically controlled process.

The morphology changes of the obtained materials were examined by SEM and TEM (Figure 5 and Figure S7). Formation of a layered silica structure with sheets of 1–1.5 μm in size was first detected at 115 °C (Figure 5a and Figure S7a). Increasing the temperature at the fixed synthesis time led to the gradual formation of larger agglomerates of thicker sheets at 160 °C (Figure 5b–e, Figure S7b). Two different phases were detected at 170 °C; according to XRD, these separate phases were attributed to magadiite and α-quartz (Figure 5e). Eventually crystalline α-quartz was obtained, reverting to the stalk-like phase made up of particles of 1–1.5 μm size (Figure 5f), which occurred at higher temperature and during prolonged synthesis.

Figure 5. SEM images of calcined silica samples after 6 days of synthesis at different temperatures: (a) 115 °C, (b) 125 °C, (c) 140 °C, (d) 160 °C, and (e) 170 °C. (f) α-Quartz synthesized after 13 days at 170 °C.

Figure 6. (a) Ar physisorption isotherms and (b) pore size distribution of calcined layered silica samples after 6 days at different synthesis temperature. The pore size distributions are calculated via the NLDFT approach and vertically offset by equal intervals of 0.011 cm³ g⁻¹ nm⁻¹.
Figure 6 depicts the Ar physisorption isotherms and the NLDFT-derived pore size distributions of the layered silica samples synthesized at different temperatures. The LS synthesized in the 115–140 °C range contains micropores \( (V_{\text{micro}} \sim 0.05 \text{ cm}^3\text{g}^{-1}) \), with a size of around 0.58 nm (Figure 6b) together with mesopores. These mesopores are quite narrowly distributed for the sample synthesized at 115 °C (2–5 nm, centered at 3.45 nm) and broadened with increasing temperature (2–9 nm) (Figure 6b). At the same time, the layered magadiite precursor (formed at 160 °C) has larger micropores (0.68 nm) and some broadly distributed additional mesoporosity \( (V_{\text{meso}} \sim 0.09 \text{ cm}^3\text{g}^{-1}) \) (Figure 6b). Also changing the degree of silica condensation through varying the synthesis temperature led to changes in the textural properties of the obtained silicas, e.g., a reduction in the BET surface area from 1183 m$^2$g$^{-1}$ at 115 °C to 65 m$^2$g$^{-1}$ at 160 °C (Table S2). The layered silica products obtained at low temperature (115–125 °C) are promising for adsorption and drug delivery because of the large surface areas (\( \sim 1000 \text{ m}^2\text{g}^{-1} \)) and the narrow distribution of mesopores.

### 3.3. Mesoporous Silica-Alumina

As a next step, we incorporated Al in the synthesis gel, in order to introduce acidic properties into the final materials. Initially, we carried out the same syntheses as above but at a Si/Al gel ratio of 100. A wide range of products, including ordered amorphous (105 °C) and partially crystallized materials (115–125 °C), were obtained upon variation of the synthesis temperature (Figure 7). The transformations were similar to those observed in the siliceous system, except for the formation of a crystalline mordenite (MOR) phase at 140 °C (Figure 7b).

SEM analysis (Figure 8) demonstrated these morphological changes with increasing temperature. Two different phases were present at 105 °C (Figure 8a), with one layered silica-alumina (AI-LS) observed at 125 °C (Figure 8c and Figure S8a) supported by XRD results. Further inspection of the samples by TEM, however, revealed the presence of the second phase on the edges of the fibrous structure at 125 °C (Figure S8a, inset). A higher synthesis temperature of 140 °C was sufficient for the formation a crystalline mordenite phase.
higher degree of silica condensation, which results in the temperature of 125°C prepared at 115 and 125°C. 15.3 were determined by ICP analysis for Al-LS samples contained a significant amount of Al. Si/Al ratios of 11.7 and 15.3 were determined by ICP analysis for Al-LS samples prepared at 115 and 125°C, respectively. 27Al NMR spectroscopy showed that the Al atoms were mainly in tetrahedral coordination in the silica matrix (>65%) (Figure 10a). The amorphous Al-LS synthesized at 105°C had a large surface area (943 m² g⁻¹) and contained uniform mesopores of ~3.3 nm (Figure 9b). A further temperature increase led to a higher degree of silica condensation, which results in the formation of materials with micropores (d = 0.58 nm, Vmic = 0.03 cm³ g⁻¹), alongside the mesoporous network. This process is accompanied by broadening of the mesopore size and a reduction of the surface area to 820 m² g⁻¹ at a synthesis temperature of 125°C (Figure 9b and Table S3).

Despite the high Si/Al ratio in the gel, the final materials contained a significant amount of Al. Si/Al ratios of 11.7 and 15.3 were determined by ICP analysis for Al-LS samples prepared at 115 and 125°C, respectively. 27Al NMR spectroscopy showed that the Al atoms were mainly in tetrahedral coordination in the silica matrix (>65%) (Figure 10a and Table S4), making them potential Bronsted acidic catalysts.

The acidic properties of the protonated form of Al-LS (125°C) sample were investigated by IR spectroscopy (Figure 11a). Two vibrational bands were observed at 3745 and 3606 cm⁻¹ in the νOH region, which can be assigned to external silanols (Si–OH) and bridging hydroxyl groups (Si–OH–Al), respectively. Pyridine was used as a probe molecule to quantify the acid sites. After pyridine adsorption at 150°C, the following characteristic signals appeared in the 1400–1600 cm⁻¹ region: the band at 1545 cm⁻¹ is due to the interaction of pyridine with strong Bronsted acid sites (BAS) and the band at 1455 cm⁻¹ relates to pyridine bonded to Lewis acid sites (LAS) (Figure 11b). The band at 1490 cm⁻¹ is assigned to pyridine molecules on both types of acid sites. After evacuation at 300°C for 1 h, we could still observe the presence of chemisorbed pyridine molecules on both types of acid sites. A BAS concentration of ~50 μmol g⁻¹ probed by pyridine after evacuation at 300°C (Table S4) is typical for amorphous silica-alumina (ASA) materials. However, at 500°C nearly no pyridine adsorbed on Bronsted acid sites was detected.

Bifunctional catalysts based on a metal such as Pt or Pd and amorphous silica-alumina are considered as an alternative to broadly used zeolite ones in the hydroconversion of n-paraffins due to their high surface area and milder Bronsted acidity suitable for obtaining middle distillates during gas oil hydrocracking. Therefore, the catalytic activity of the Al-LS sample was compared to a commercial amorphous silica-alumina (Com-ASA) in the hydroconversion of n-hexadecane. The two samples exhibited similar acidic properties (Table S4). Prior to the activity tests, the protonated forms of the amorphous silica–alumina were loaded with 1 wt % Pd followed by calcination at 450°C in air. The results of H₂ chemisorption after reduction (Pd dispersion) and the BAS concentration (Table S4) confirmed an adequate balance between the metal and acid sites. This ratio of metal hydrogenation sites to BAS is sufficient for acid-catalyzed reactions to be rate-controlling in the overall hydroconversion reaction. The conversion of n-hexadecane as a function of temperature is shown in Figure 12a. The Pd/Al-LS catalyst displayed a lower apparent activation energy (163 kJ/mol) than the commercial counterpart (188 kJ/mol) (Figure 12b).

The samples exhibited similar catalytic behavior, namely, a low selectivity to cracking products up to n-hexadecane conversion of 80% (Figure 12c), explained by the relatively weak acidity of the amorphous materials (Table S4). The Pd/Com-ASA displayed a slightly “M-shaped” distribution of...
cracked product (Figure 12d), whereas the Pd/Al-LS sample showed a more symmetric distribution of cracked products at 50% conversion. The latter distribution is closer to the cracking pattern expected for the ideal hydrocracking regime.55 Taking into account the similar concentration of Brønsted acid sites (BAS $\sim 45 \mu$mol/g) and a proper amount of Pd per acid sites, we associate the improved catalytic performance of the Pd/Al-LS material to its more beneficial textural properties. This can also be supported by the smaller size of the Pd particles (determined by CO chemisorption) for Pd/Al-LS sample ($\sim 1.1$ nm) in comparison with Pd/Com-ASA ($\sim 3.5$ nm). A shorter distance between the two catalytic functions can lead to a lower contribution of secondary cracking on BAS,52,56 in agreement with the bifunctional hydrocracking mechanism.57-58 The used Pd/Al-LS and Pd/Com-ASA samples were additionally tested in their ability to reach 40% conversion at the same temperature as the fresh one (Figure 12a). The catalysts showed comparable activity during the second run.

3.4. Hierarchical MOR Nanorods. In the previous section, we observed the formation of mordenite crystals in the sample synthesized at 140 °C after the introduction of aluminum source into the gel. In order to obtain a fully crystalline zeolite phase, a higher Al content is needed because MOR zeolite is typically synthesized with Si/Al ratio of around 7-10.59,60 We started with a Si/Al ratio of 20, which is relevant...
for crystallization of mordenite assisted by imidazolium salts and Na+ ions. XRD analysis showed the typical diffraction pattern of MOR (Figure S9a). However, SEM images revealed the presence of an additional amorphous phase (Figure S9b). Gradually increasing the Al content to Si/Al ratios of 15 and 10 resulted in the formation of highly crystalline mordenite (Figure S10), denoted as MMOR-15 and MMOR-10, respectively. The complete conversion into crystalline MOR took place after 6 days of the synthesis at 140 °C as confirmed by SEM and TEM analysis (Figure 13 and Figure 14) of the products after 6 days of the synthesis at 140 °C. Along with these hierarchically porous zeolite materials, conventional bulk analogues were also synthesized by the same method but without addition of an organic SDA (MOR-15 and MOR-10).

Both samples obtained in the presence of C16dMImz consist of uniform crystals of 2−2.5 μm size (Figure 13a,b), while the microporous references appeared differently. MOR-15 had uniform particles with a smooth surface (4−4.5 μm) and MOR-10 contained typical prism-shaped crystals together with deformed smaller ones (Figure 13c–e). Further, the TEM images of MMOR-15 revealed a complex structure, which consisted of stacked nanorods with a width of ~20 nm, separated by mesoporous voids (Figure 13c). An observed lattice distance of 1.33 nm is attributed to the [110] plane (Figure 13c, insert) and points to nanorods oriented parallel to the c-axis. As discussed in our previous work, the hydrophilic head group of the SDA molecule is likely located in the 8MR side-pockets or at the interface between the 8MR and 12MR channels, while the hydrophobic tail is blocking crystal growth in the a- and b-directions. Ar physisorption results for the products synthesized in the presence of C16dMImz display the type IV isotherm, whereas the conventional MOR-15 and MOR-10 samples have the type I isotherm, which is typical for exclusively microporous materials (Figure 14a). The hierarchical mordenite products were highly crystalline (V_{micro} 0.11−0.12 cm$^3$ g$^{-1}$) and characterized by a small volume of mesopores (0.08−0.09 cm$^3$ g$^{-1}$) combined with a large external surface area (70.4−

![Figure 13. SEM (a,b,d,e) and TEM (c,f) images of calcined MOR zeolite samples: (a,c) MMOR-15, (b) MMOR-10, (d,f) MOR-15, and (e) MOR-10.](image)

![Figure 14. (a) Ar physisorption isotherms and (b) pore size distribution of calcined MOR samples. The isotherms are offset for clarity by 50 cm$^3$ g$^{-1}$. The pore size distributions are calculated via the NLDFT approach and vertically offset by equal intervals of 0.005 cm$^3$ g$^{-1}$ nm$^{-1}$.](image)
79.7 m² g⁻¹ (Table S5). The pore size distributions derived from the NLDFT-method showed that uniform pores of ~5.5 nm in size were formed in all the mesoporous MOR materials (Figure 14b).

As typical for MOR, Si/Al ratios of 7 ± 0.5 were observed for the all materials.²⁷ Al NMR spectra displayed a high degree of Al incorporation into the framework (>75%) (Figure 15 and Table S6). The spectra also showed a broad peak at ~0 ppm, which can be attributed to the extraframework aluminum (EFAl) species.⁶⁵

Considering the small differences regarding the crystallinity and textural properties between the hierarchical MOR samples, we selected mMOR-15 for further characterization and catalytic testing. Along with external silanols (Si–OH) and the bridging hydroxyl groups (Si–OH–Al) observed in the silica-alumina (Figure 11a), the mordenite samples displayed features such as internal silanols at 3733 cm⁻¹ (MOR-15) and the band at 3658 cm⁻¹, assigned to OH groups connected to extraframework aluminum (EFAl) (Figure 16).⁶⁶ The fact that the number and apparent strength of the Brønsted acid sites increased, when compared to the layered products, was supported by the retention of some BAS, even after pyridine desorption for 1 h at 500 °C (Figure S11 and Table S7). The decreased amount of BAS (~30%) available for a bulk pyridine molecule in the mMOR-15 sample can be attributed to the reduced number of acid sites located in the main 12 MR channels, due to a particular Al distribution in the presence of C₁₆dMImz. We have observed similar behavior in our previous work, where MOR nanorods were synthesized in the presence of a pyrrolidine-based mesoporogen.²⁷

Hierarchical zeolites are promising catalysts for Friedel–Crafts alkylation/acylation reactions with bulky reactants and/or products due to their strong acidity and the presence of a second level of porosity, which helps to overcome the diffusion limitations.⁵⁷–⁶⁹ We evaluated the obtained MOR zeolites in the model alkylation reaction of benzene (B) with benzyl alcohol (BA) that leads to diphenylmethane (DPM) in the presence of acid forms of MOR-15 and mMOR-15 catalysts (Scheme S1). The activity tests were carried out at 80 °C and under stirring (900 rpm).⁷⁰ Figure 17 displays the conversion of benzyl alcohol as a limiting reagent (B/BA 50 mol/mol) as a function of the reaction time. While conventional MOR did not display any BA conversion to the products even after 30 h of the reaction, the conversion of BA over hierarchical MOR reached 14.5% (selectivity DPM 58%). Since both catalysts contain a comparable amount of acid sites, we attribute the very different catalytic behavior to the improved textural and diffusion properties of the mesoporous MOR sample.

The one-dimensional channel system of MOR is characterized by a pore size of 6.5 Å × 7.0 Å. This size is smaller than necessary for the transition state of the studied benzylation reaction.⁷⁰ This leads to a low activity of the exclusively microporous MOR catalyst. As TEM results showed mMOR-15 sample has additional pores of 5.5 nm running along the c-axis, together with the microporous channels. The enhanced catalytic activity of hierarchical mordenite can therefore be explained by the reaction taking place at the mesopore walls and/or on BAS located in the micropore openings, accessible for BA through the mesoporous network. This conclusion is also supported by other studies,⁵⁷,⁷⁰ where hierarchical mordenite catalysts displayed enhanced performance in similar reactions.

4. CONCLUSIONS

In this work, we described the synthesis of several mesoporous materials such as amorphous silica and silica-alumina and crystalline zeolites, using C₁₆dMImz as a single SDA. Controlling the degree of silica condensation, by changing the temperature, allowed the tuning of the textural and morphological properties (surface areas in the 65–1200 m² g⁻¹ range) of silica. When aluminum is introduced, two types of acidic materials can be obtained, i.e., ordered silica-alumina...
with weak Brønsted acid sites and hierarchical mordenite zeolite with strong Brønsted acid sites. These acidic catalysts displayed promising catalytic performance in the hydroisomerization of \( n \)-hexadecane with \( \text{Pd/AL-LS} \) and the Friedel–Crafts alkylation of benzene with benzyl alcohol with MOR zeolite.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b15593.

Additional characterization data including XRD patterns, EM images, results of liquid and solid NMR, Ar physisorption, elemental analysis, and IR after pyridine desorption (PDF)

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**Notes**

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