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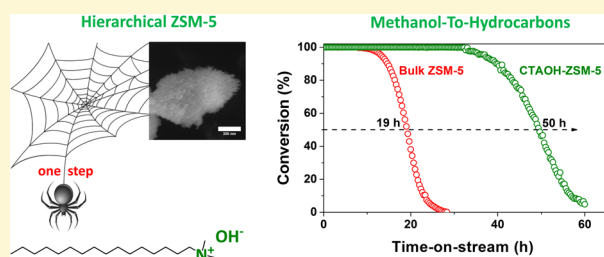
One-Step Synthesis of Hierarchical ZSM-5 Using Cetyltrimethylammonium as Mesopore and Structure-Directing Agent

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Supporting Information

ABSTRACT: Hierarchical ZSM-5 zeolite is hydrothermally synthesized in a single step with cetyltrimethylammonium (CTA) hydroxide acting as mesopore and structure-directing agent. Essential to this synthesis is the replacement of NaOH with KOH. An in-depth solid-state NMR study reveals that, after early electrostatic interaction between condensed silica and the head group of CTA, ZSM-5 crystallizes around the structure-directing agent. The crucial aspect of using KOH instead of NaOH lies in the faster dissolution of silica, thereby providing sufficient nutrients for zeolite nucleation. The hierarchical ZSM-5 zeolite contains mesopores and shows excellent catalytic performance in the methanol-to-hydrocarbons reaction.



INTRODUCTION

In catalysis, molecular confinement can be a bliss or a woe. Zeolites, crystalline aluminosilicates with inherent acidity that contain well-defined pores and pore windows, are a case in point. Only molecules that fit in the pores may form during a catalytic cycle, and only those molecules that can move through the pore windows are allowed to leave the scene of catalysis.¹ But molecular diffusion suffers from confinement. A notorious problem in industrial catalysis, such diffusional limitations may leave a large fraction of acid sites within a zeolite crystal unused. The consequences on overall performance are usually crippling: low overall efficiencies and undesired secondary reactions, such as coking, lead to lower conversion rate and rapid deactivation of the catalyst.^{2–4}

Hierarchically organized zeolites are materials in which wider pores are integrated in crystalline microporous zeolites.^{5–12} The additional porosity can be placed within or between zeolite crystals. Pérez-Ramírez and co-workers demonstrated that there is no need for the additional pore network to be ordered to achieve the desired improved catalytic performance.^{13–17} In search of one-step synthesis of hierarchical zeolites by a soft-templating strategy, progress has come from the use of amphiphilic organic structure-directing agents (SDAs). The approach to ZSM-5 zeolite nanosheets involves enforced silica–head group interaction by diquaternary ammonium surfactant (DQAS) SDAs developed by Ryoo's group.^{18,19} These SDAs are made by multiple alkylation steps, which makes them too expensive for industrial application. Relatively inexpensive methods for hierarchical zeolite synthesis do exist, most notably the repetitive branching of nanosheets in a one-pot synthesis.²⁰

Attempts at using cetyltrimethylammonium (CTA)—a similar amphiphilic template with a single quaternary ammonium head

group—as SDA for hierarchical zeolites have been unsuccessful; the resulting silicates, such as MCM-41, are ordered at the mesoscale, but lack crystallinity and acidity.^{21–23} Experiments using mixtures of CTA and small SDAs such as tetrapropylammonium are numerous, but have invariably lead to physical mixtures of ZSM-5 and MCM-41.^{24,25} Seed-based approaches using CTA work out well.^{26–28} Recently, bulk ZSM-5 was synthesized successfully in one step using CTABr as surfactant.^{29,30}

Yet, the question remains what obstructs obtaining mesoporous ZSM-5 with CTA directly. In explaining the difference between Ryoo's DQAS SDA and CTA, Zhu et al. recently showed that CTA's quaternary ammonium head group fails to enter the inorganic matrix from the very onset of silica condensation.³¹ In the late 1980s, Wijnen et al. found that dissolution of silica gel is suppressed by tetramethylammonium. The authors showed that silica dissolution can be drastically enhanced by using KOH instead of NaOH.^{32–35} Following this, we replaced NaOH by KOH and decreased the CTA/SiO₂ ratio in the gel to obtain highly crystalline hierarchical ZSM-5 zeolites in a single step by hydrothermal synthesis. To the best of our knowledge, this is the first time that CTA is reported to simultaneously act as mesopore and SDA, in zeolite synthesis.

EXPERIMENTAL SECTION

Synthesis. Hierarchical ZSM-5 zeolite was synthesized as follows: 0.299 g of KOH (Aldrich, 90%) and 3.350 g of CTAOH solution (TCI, 10 wt %) were added to 11.085 g of demiwater at room temperature. Afterward, 0.033 g of aluminum hydroxide (Aldrich, St. Louis)

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and 3.167 g of Ludox AS-40 (Aldrich, 40 wt %) were added to the mixture under vigorous stirring. The final gel had a molar composition of $K_2O:SiO_2:Al_2O_3:CTA:H_2O = 12:95:0.95:5:4000$. After stirring at room temperature for 2 h, the resulting gel was transferred into a 45 mL Teflon-lined steel autoclave and heated under rotation (50 rpm) at 413 K for 6 days. After crystallization, the white product was filtered and washed with demineralized water followed by drying overnight at 383 K (1.31 g of zeolite). This zeolite was calcined at 823 K for 10 h under flowing air to remove the surfactant. The calcined zeolite (1.07 g) was ion-exchanged three times with 1.0 M NH_4NO_3 solutions followed by calcination at 823 K for 4 h in flowing air to obtain the final proton form (0.95 g). This zeolite is denoted as CTAOH-ZSM-5. A similar synthesis was performed using NaOH at the same NaOH/SiO₂ ratio. For comparison, bulk ZSM-5 zeolite was synthesized using tetrapropylammonium hydroxide (TPAOH, Merck, 40 wt %) as template.

Characterization. X-ray diffraction patterns (XRD) were recorded on a Bruker D4 Endeavor diffractometer using Cu K α radiation with a scanning speed of $0.02^\circ s^{-1}$ in the 2θ range of $5-40^\circ$ and $0.004^\circ s^{-1}$ in the 2θ range of $0.7-5^\circ$.

Ar Physisorption. Surface area and porosity of zeolites were determined by Ar physisorption in static mode at 87 K on a Micromeritics ASAP 2020 instrument. The zeolites were outgassed at 723 K for 6 h prior to the sorption measurements. The pore size distribution (PSD) was determined by NLDFT method (Ar at 87 K assuming slit pores without regularization).

Electron Microscopy. Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200F scanning electron microscope at an accelerating voltage of 5 kV. 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 with a film prior to measurements.

NMR Spectroscopy. Nuclear magnetic resonance (NMR) spectra were measured using a 11.7 T Bruker DMX500 NMR spectrometer operating at 500 MHz for 1H , 99 MHz for ^{29}Si , 125 MHz for ^{13}C , and 132 MHz for ^{27}Al . All NMR experiments were performed using a Bruker Triple Channel 4 mm MAS probe head spinning at 10 kHz. 1H NMR spectra were recorded with a Hahn-echo pulse sequence $p1-\tau1-p2-\tau2-aq$ with a 90° pulse $p1 = 5 \mu s$ and a 180° pulse $p2 = 10 \mu s$. The interscan delay was chosen as 5 s. Two-dimensional $^1H-^{29}Si$ and $^1H-^{27}Al$ heteronuclear correlation (HETCOR) were recorded with a ramped contact pulse of 3 ms. During the acquisition, 1H heteronuclear decoupling was applied using the spinal-64 pulse scheme. 1H and ^{29}Si NMR shifts were calibrated using tetramethylsilane (TMS). Saturated $Al(NO_3)_3$ solution and solid adamantane were used for ^{27}Al and ^{13}C NMR shift calibration, respectively.

Catalytic Activity Measurements. The catalytic activity of ZSM-5 zeolites in the methanol-to-hydrocarbons reaction was tested in a quartz tubular fixed-bed reactor with 4 mm inner diameter. Typically, an amount of proton form of ZSM-5 zeolite was pressed and sieved into 250–425 μm particles. Prior to the reaction, the catalysts were calcined at 823 K in 20 vol % O_2 in He ($30 mL \cdot min^{-1}$) for 4 h. The methanol-to-hydrocarbons reaction was performed at 673 K. Methanol (Merck, 99%) was introduced to the reactor by passing a He flow of $30 mL \cdot min^{-1}$ through a thermostated saturator. The WHSV of methanol was kept at $6 h^{-1}$. The product effluent was analyzed online by gas chromatography (an Interscience Compact GC equipped with TCD and FID detectors with RT-Q-Bond and Al_2O_3/KCl columns). Dimethyl ether was used as reactant in the reaction.

RESULTS AND DISCUSSION

Figure 1 shows that crystalline hierarchical ZSM-5 zeolites can be obtained after 6 days of autoclaving at 413 K with commercially available CTAOH. The same synthesis using NaOH yields an amorphous product (Figure S1 of the Supporting Information). The XRD pattern of the fully crystallized zeolite after 6 days, and also the relative intensity ratios of dominant (011), (200), (031), and (051) reflections are practically unchanged with regard to those obtained for bulk MFI. This indicates that

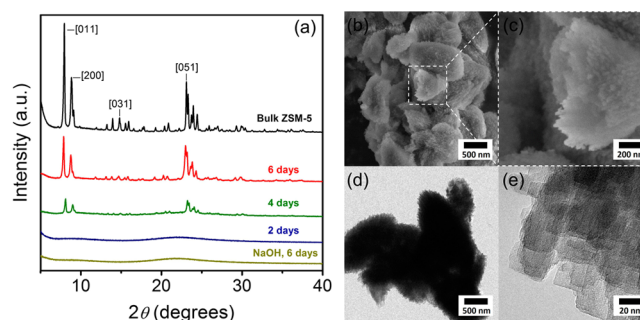


Figure 1. (a) XRD of the as-synthesized CTAOH-ZSM-5 from a composition gel of $K_2O:SiO_2:Al_2O_3:CTA:H_2O = 12:95:0.95:5:4000$, and comparison to bulk MFI, and a sample synthesized with NaOH; (b and c) SEM and (d and e) TEM images of CTAOH-ZSM-5.

CTAOH does neither promote nor inhibit certain crystallographic planes of ZSM-5 in synthesis, an effect associated with *molecular recognition*.

Probing for larger d -spacings in the low-angle part of the XRD pattern (Figure S2), we found a broad reflection. Although too diffuse to reasonably relate to any sort of repetitive symmetry, it is a hint at low-order secondary structuring at the mesoscale. SEM (Figure 1b,c) and TEM (Figure 1d,e) analyses of CTAOH-ZSM-5 indicate an agglomeration of nanosized crystals.

Before exploring the texture in more detail, we focus on the peculiar effect of combining KOH with low concentration of CTA. A thorough MAS NMR study was carried out, focusing on the evolution of NMR patterns of the 1H , ^{13}C , ^{29}Si , and ^{27}Al nuclei. The structure was studied in detail by two-dimensional $^1H-^{29}Si$ HETCOR and $^1H-^{27}Al$ MAS NMR (single-dimension data in Figures S3 and S4). These two experiments are highly suitable for mechanistic studies on SDA–silicate interactions, as they can reveal proximities of CTAOH H's to (proto)zeolitic Si's,^{36,37} and as will be shown, the temporal evolution of that vicinity.

The 2D spectra are shown in Figure 2. The top row displays three $^1H-^{29}Si$ HETCOR MAS NMR spectra, taken after 2, 4, and 6 days. The 1H and ^{29}Si single-dimension spectra are represented twice: in blue projections from the 2D plot and in black 1D cross-polarization spectra. The black curves give a high-resolution representation of the chemical nature of the species present, but they should not be interpreted in quantitative fashion. As can be seen, the single ^{29}Si dimension shows the presence of both Q_3 and Q_4 ^{29}Si (the subscript denotes the number of bridging O's). The significant presence of a Q_3 ^{29}Si resonance represents a sign of incomplete condensation. The 2D correlation, for 2 days of synthesis (Figure 2a), is as expected: intense cross peaks are observed between CTA's head group and the silicate, which at this stage is amorphous (see Figure 1). In Figure 2, an inset is placed to denote the 1H resonances of CTA. We will refer to the methylene protons closest to the head group, with their detectable resonance, as β -methylene. The absence of correlation between ^{29}Si and β -methylene 1H from CTA indicates that the latter's head group is not settled within the silica. So at this stage, structure direction appears as a no-go, but the situation changes.

After 4 days (Figure 2b), Q_4 intensifies with respect to Q_3 , a sign of further condensation. XRD showed that bulk crystallization has well begun and proceeded. In the 2D spectrum, new correlations appear. Perhaps initially appearing as a single large cross peak, closer inspection reveals (at both sides in the

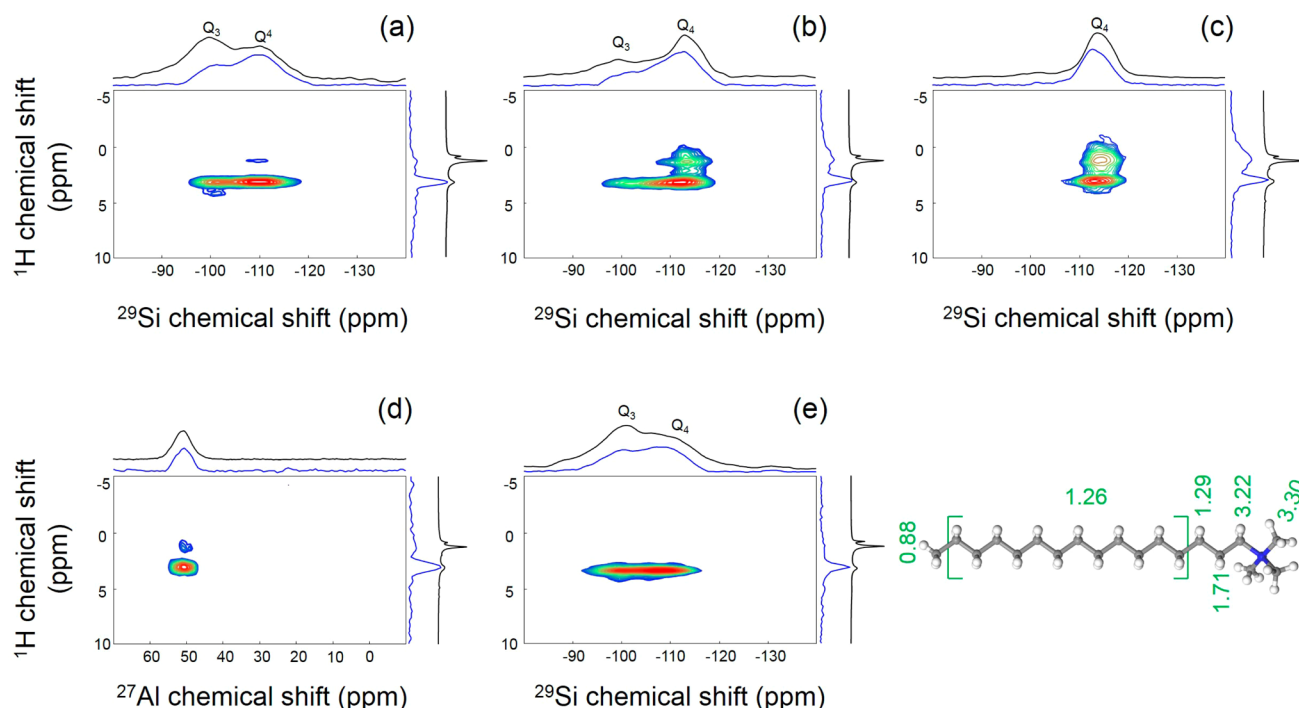


Figure 2. MAS NMR experiments. The molecule, inserted in the bottom right corner, shows the documented ^1H chemical shifts of CTA, to act as a guideline for the ^1H dimension in all 2D spectra. The top three graphs show ^1H - ^{29}Si HETCOR spectra of CTAOH-ZSM-5 after (a) 2 days, (b) 4 days, and (c) 6 days; (d) ^1H - ^{27}Al HETCOR spectrum of CTAOH-ZSM-5 after 6 days of synthesis; and (e) ^1H - ^{29}Si HETCOR spectrum of the sample after 6 days, with NaOH instead of KOH in synthesis.

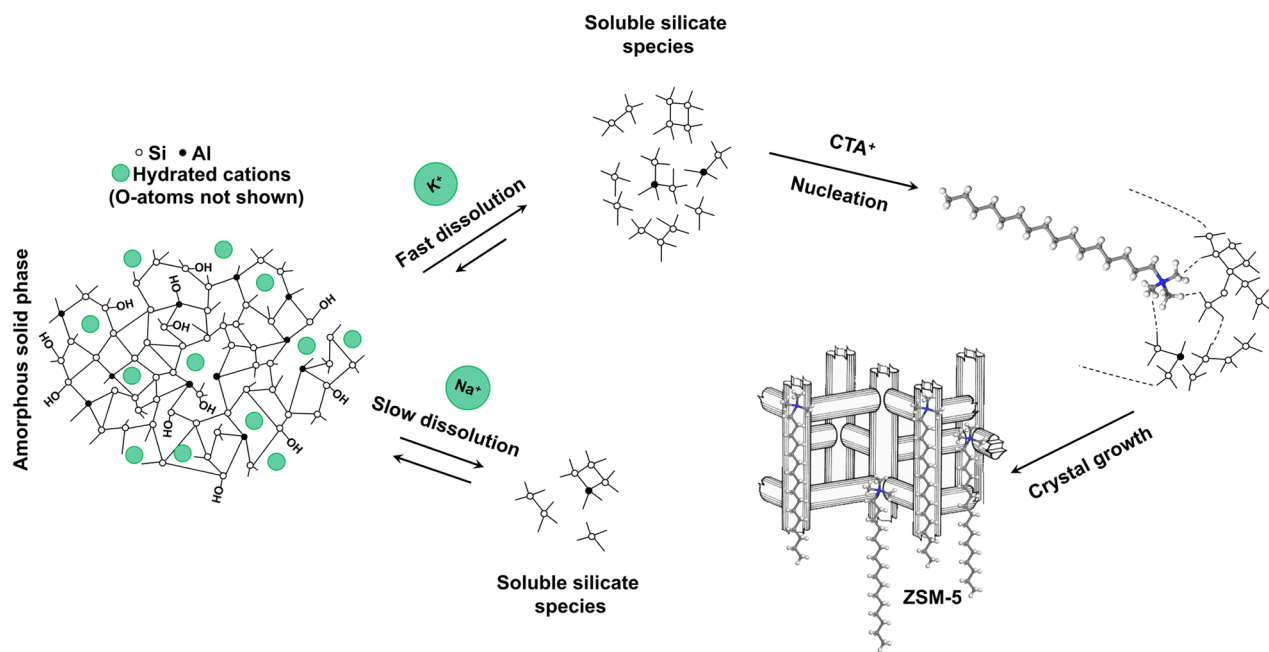


Figure 3. Mechanism of hierarchical ZSM-5 zeolite formation in the presence of CTAOH and KOH, and amorphous silica formation in the presence of NaOH.

^1H dimension) cross peaks for the terminal methyl, and β -methylene of the hydrophobic tail. ZSM-5 has crystallized around CTA's entire tail.

This is also supported by the changes observed in the 1D ^1H - ^{13}C CPMAS NMR spectra (Figure S5). These bring all CTA's ^{13}C resonances in high resolution. After 2 days of synthesis, the methyl ^1H 's of CTA's tail are not visible. This has been noted before, and is an effect of high molecular mobility

preventing efficient ^1H - ^{13}C cross polarization.³⁸ But after 4 days, the signal is there, indicating a reduced mobility for the terminal methyl group, which has become encapsulated by the zeolite. Returning to the 2D ^1H - ^{29}Si experiment, it is further noted that there is an absence of cross peaks between Q_3 ^{29}Si and CTA's tail ^1H 's. This indicates that the hydrophobic part of the SDA resides within the bulk of crystallizing CTAOH-ZSM-5, and not (exclusively) near the crystal surface.

Toward the end of synthesis, after 6 days (Figure 2c), the Q_3 ^{29}Si resonance has become marginal (although still there, Figure S3). At this stage, only surface ^{29}Si 's, of the ZSM-5 crystals, give rise to this signal. The signals in both 1D and 2D dimensions have sharpened, indicating a high degree of molecular ordering, the sign of a crystalline material. The same picture can be sketched from the perspective of 1D ^{27}Al experiments (Figure S4): a sharpening of the ^{27}Al signal indicates progressive order with time. A ^1H - ^{27}Al HETCOR MAS NMR experiment taken after 6 days (Figure 2d) corroborates this: two sharp cross peaks indicate close distances between Al and CTAOH. There appears no preferential location for aluminum, as it correlates with both the tail and head group of CTA.

On the basis of Figure 2e, the importance of using KOH instead of NaOH is to be stressed again. As seen from Figure 2e, 6 days of an analogous synthesis, with NaOH instead of KOH, produces a dominant Q_3 signal (incomplete condensation) and there is only correlation between CTA's head group protons in the 2D plot. Clearly, for Si to dissolve from the amorphous silicate source, and interact with CTA, KOH is required.

A tentative mechanism explaining the chain of events leading to formation of mesoporous ZSM-5 is depicted in Figure 3. As usually the case, crystallization here is preceded by formation of an amorphous gel phase in which the negatively charged silicate surface is compensated by alkali cations. In line with literature^{32–35} and as shown above, K^+ (instead of Na^+) favors dissolution of silicate species from this amorphous solid. This is crucial, for primary nucleation is driven by supersaturation of silicate species in the solution. The importance of CTAOH in the nucleation step relates to the observation that no crystalline zeolite could be obtained in a similar synthesis without CTAOH (Figure S6). CTA's hydrophobic tail limits crystal growth, resulting in final hierarchical material. To further support the hypothesis that nucleation is indirectly inhibited by Na^+ , a small amount of bulk H-ZSM-5 zeolite seed crystals was added to the synthesis gel. In this case, (secondary) nucleation proceeded toward a similar material, just as obtained with KOH, without seeds (Figure 4 and Figure S7). Finally, it was observed

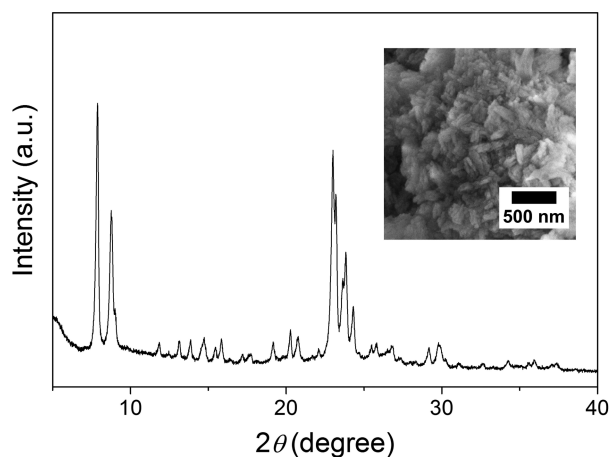


Figure 4. XRD pattern and SEM image (inset) of the as-synthesized ZSM-5 from a composition gel of $\text{Na}_2\text{O}:\text{SiO}_2:\text{Al}_2\text{O}_3:\text{seed}:\text{CTA}:\text{H}_2\text{O} = 12:95:0.95:5:5:4000$.

that, in an all-silica synthesis, needlelike ZSM-48 (MRE; one-dimensional 10MR pore system) was obtained instead of ZSM-5 (Figure S8).³⁹

In Ar physisorption, CTAOH-ZSM-5 displays a hysteresis loop, and a climbing slope at the intermediate pressure range (Figure 5a). The loop does not close until the equilibrium

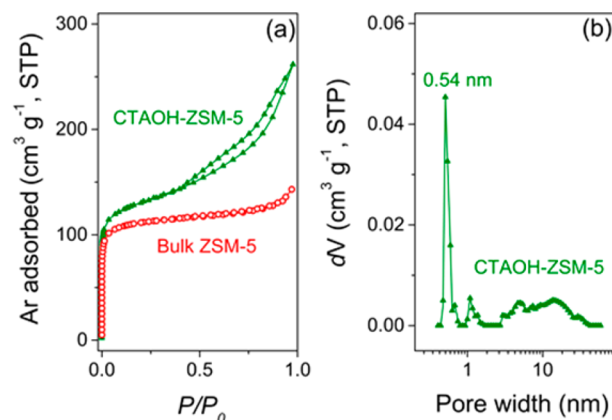


Figure 5. (a) Ar physisorption isotherm of CTAOH-ZSM-5 and bulk ZSM-5, and (b) the corresponding pore size distribution, calculated by the NLDFT method.

pressure is very close to the saturation pressure. In terms of IUPAC classifications, the isotherm is of the H4 type.⁴⁰ From the shape of the isotherm, we infer that a complex, hierarchical material containing micropores and mesopores was obtained.⁴¹ In comparison to bulk ZSM-5, additional micropores are present, evident from the strong uptake at very low pressures. As common estimations for the pore size distribution (PSD) such as the BJH method are considered unreliable for the H4 type of isotherm,⁴¹ the NLDFT method was applied, assuming slit-shaped pores (Figure S9). The computed PSD displayed in Figure 5b confirms the existence of an additional set of micropores, next to the micropore system of ZSM-5, centered at 0.54 nm. There is also a broad set of larger pores, stretching into the mesopore regime, from 2 to 40 nm. The corresponding textural properties are listed in Table S1. The shape of the PSD, as well as the documented fact that H4 isotherms are typically observed for aggregates of nanosized zeolite crystallites,⁴² fits our SEM and TEM analysis. The combination of microscopy and sorption thus suggests that the secondary (larger) set of pores in CTAOH-ZSM-5 originates from voids between intergrown nanocrystals.

The catalytic performance of CTAOH-ZSM-5 was compared with bulk ZSM-5 in the methanol-to-hydrocarbons (MTH) reaction, a stock reaction in the field of hierarchically organized zeolites and important to an oil-independent future.⁴³ The currently employed zeolite catalysts for that process suffer from premature deactivation due to coking, which appears as a result of diffusional limitations. CTAOH-ZSM-5's acting as acid catalyst is displayed in Figure 6. It is clear that CTAOH-ZSM-5's longevity as catalyst is excellent, with significant decline in performance only occurring after 50 h. For comparison, this happens for bulk ZSM-5 already after 19 h. The product selectivities of the two zeolites are similar, which suggests that reaction mainly takes place within the micropores (Table S2). Since the Brønsted acidity in CTAOH-ZSM-5 is similar in strength and number, as compared to bulk ZSM-5 (Figure S10 and Table S3), we conclude that additional porosity enhances the catalytic performance.

In summary, we propose a new one-pot synthesis of hierarchical ZSM-5 based on CTAOH and KOH. Both chemicals are

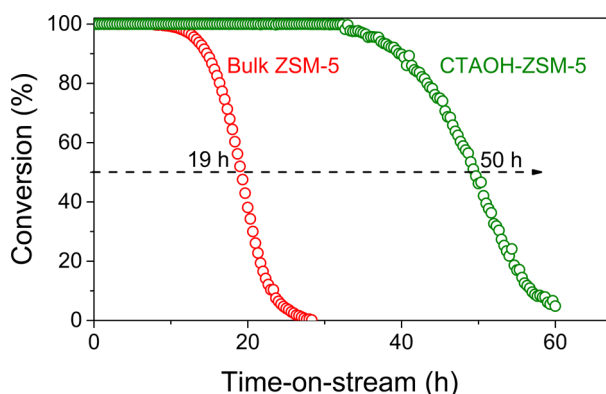


Figure 6. Performance of CTAOH-ZSM-5 as catalyst in methanol-to-hydrocarbons reactions compared to bulk ZSM-5.

commercially available and involve a facile upgrade with respect to established synthesis to bulk zeolite.

The replacement of NaOH by KOH, to facilitate dissolution of silicate from an amorphous condensed precursor, is thought-provoking. And we believe it is worthy of further exploration, possibly finding extension to a broader range of zeolite topologies, and hierarchical architectures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.7b00913](https://doi.org/10.1021/acs.chemmater.7b00913).

Detailed information regarding XRD, Ar physisorption, FTIR spectroscopy, electron microscopy, elemental analysis, NMR spectroscopy, and products selectivities in methanol conversion (PDF)

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Notes

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