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Syntheses of High-Silica Zeolites in Urea/Choline Chloride Deep Eutectic Solvent

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ABSTRACT: This paper presents the first example of high-silica and siliceous zeolite synthesis in the urea/choline chloride mixture as a deep eutectic solvent (DES), using F^- as the mineralizing agent. Urea/choline chloride mixture was previously used as solvent to prepare $AlPO_4$ -based microporous materials SIZ-2 and $AlPO-CJ2$. However, generating these materials depends on the formation of ammonium ion as structure-directing agent (SDA) that is the side product of urea decomposition. In the present study, we show that several highly siliceous zeolites with targeted topologies (MFI, BEA, MEL, MTN) can be purposely synthesized by adding SDAs of choice rather than relying on solvent decomposition. The Si atoms in zeolite Beta synthesized in urea/choline chloride mixture exhibit exceptionally high local ordering as shown in ^{29}Si MAS NMR spectrum. The synthesis of ZSM-11 using eutectic solvents or ionic liquid has not been reported. The major challenge in ZSM-11 synthesis is the intergrown structure formed with ZSM-5 due to the high similarity in their topologies. The present work shows that preparation of pure ZSM-11 can be achieved in urea/choline chloride DES using either DPHMII or DECDMPI as SDA. Using urea/choline chloride mixture rather than alcohol based traditional non-aqueous solvents is the key for the success of preparing phase-pure ZSM-11 free of any MFI intergrowths. This is because some alcohols can serve as SDA for MFI. The use of urea/choline chloride based DES eliminates the potential templating effect of solvent for MFI formation. For MTN zeolite, morphology may be controlled in

urea/choline chloride by choosing different SDAs. The disadvantage of this system is the long reaction times.

Introduction

Zeolites, which are three-dimensional framework aluminosilicates and silicates, are extremely important in industry for their roles in catalysis, ion-exchange, adsorption and gas separation/purification.¹ Much effort has been put in for the investigations in different synthetic routes in order to discover new types of zeolite or zeolite-like microporous materials. Hydrothermal synthesis is the most commonly used method for zeolite synthesis. Recently, Morris *et al.* pioneered a new synthetic approach termed ionothermal synthesis where an ionic liquid (IL) or a deep eutectic mixture is used as a solvent in the syntheses of microporous materials. As solvents for preparation of zeolites or zeolitic materials, the ILs and deep eutectic mixtures (also known as deep eutectic solvents, DESs) usually need to have a melting point in the temperature range of around 150-200 °C at which most zeolites and zeolitic materials crystallize.²

One of the main advantages of using an IL or a DES for synthesis is that the solvent molecules can act as both the solvent and the organic structure-directing agent (SDA). Ideally, this lowers the competition for the SDA between the solvent and the growing framework during crystallization.² Indeed, ionothermal synthesis has been successfully used to synthesize several types of microporous materials such as AlPO_4 -, GaPO_4 - and SAPO-based molecular sieves as well as metal-organic frameworks with existing or novel topologies.³⁻¹⁰ However, there have been relatively few reports on the preparation of siliceous zeolites mainly due to the poor solubility of silica in the ILs and DESs.^{5, 8-15} So far, to the best of our knowledge, there are only six reports on ionothermal syntheses of zeolites.^{5, 9-11, 13-16} In most cases^{5, 8-15}, a small amount of water was always added to the reaction mixture for ionothermal synthesis as the presence of water is essential for the

reactions to take place. Water plays crucial roles in the dissolution of reactant species and the condensation steps of the framework formation.¹³

The present work focuses on the ionothermal preparation of several representative high-silica zeolites with different topologies in a DES of urea/choline chloride by using different organic SDAs, depending on the target framework. We show that zeolites ZSM-5 (MFI), ZSM-11 (MEL), zeolite Beta (BEA), and ZSM-39 (MTN) can be synthesized in a 2:1 mole ratio of the urea/choline chloride DES. The preparation of ZSM-5 and BEA required the presence of 5% calcined seeds, while the other reactions are non-seeded. All syntheses were performed using fluoride as the mineralizing agent. MFI, MEL, and MTN were prepared using colloidal silica as the silica source, while the silica source for BEA is fumed silica. The organic structure directing agents (SDAs) used to synthesize MFI, MTN, and BEA are tetrapropylammonium bromide (TPABr), tetramethylammonium chloride (TMACl), and tetraethylammonium hydroxide (TEAOH), respectively. The syntheses of MEL was performed under different conditions using different organic SDA: *N*, *N*-dipropylhexamethyleneiminium iodide (DPHMII) and *N,N*-diethyl-3, 5-dimethylpiperidinium iodide (DECDMPI) (Figure 1). 5% of calcined siliceous ZSM-11 was added to the initial reaction mixture for the synthesis involving DECDMPI. All as-synthesized zeolites are phase-pure. Furthermore, the synthetic approach described only requires a minimum amount of water, which exclusively comes either from the source of silica or SDA (specifically TEAOH).

Experimental

Syntheses of high-silica zeolites

All reactions were performed in stainless steel autoclaves that are placed in an oven at a temperature of 140 °C unless otherwise stated. The amount of colloidal silica Ludox HS-40 added to each reaction batch was 2.5 g.

Urea/Choline Chloride Mixture

The 2:1 mole ratio of urea/choline chloride mixture is prepared by mixing urea (99.0-100.5%, Sigma-Aldrich) and choline chloride ($\geq 98.0\%$, Sigma-Aldrich).

Synthesis of Siliceous ZSM-5 Zeolites (Silicalite-1)

The typical procedure is as follows: Ammonium fluoride ($\geq 98\%$, Alfa Aesar), tetrapropylammonium bromide (98%, Sigma-Aldrich), and dry calcined ZSM-5 (from hydrothermal synthesis using TPABr) were mixed together with urea and choline chloride quantitatively and ground using a mortar and pestle. The ground solid mixture was then transferred to a 40 mL Teflon container. To this mixture, a source of colloidal silica, (Ludox HS-40, Sigma-Aldrich) was added. The components were hand-mixed using a spatula until a sticky white paste is formed inside the Teflon cup. The Teflon container was then placed inside a stainless steel autoclave and the reaction mixture was heated at around $140\text{ }^{\circ}\text{C}$ for 19-26 days. For every 2.5 g of Ludox HS-40 (colloidal silica containing 40% SiO_2 and 60% H_2O), 0.36 g TPABr, 1.9 g urea, 2.2 g choline chloride, 0.62 g NH_4F , and 0.05 g calcined MFI seeds were mixed and ground. Ludox HS-40 was then added to the mixture. Each 2.5 g of Ludox HS-40 contains 1.0 g SiO_2 and 1.5 g H_2O . The typical molar composition of the initial batch is: 1.0 SiO_2 : 1.0 NH_4F : 0.08 TPABr: 1.9 urea: 0.95 choline chloride: 5.0 H_2O . The final weight of the zeolite produced was 0.56 g for 2.5 g of Ludox HS-40 in the initial reaction mixture.

Syntheses of Zeolite Beta

In the synthesis of BEA, tetraethylammonium hydroxide (40.0%, Sigma Aldrich) was used as the SDA, and fumed silica (AEROSIL®300, Degussa) was used, instead of Ludox HS-40. 0.05 g of calcined BEA were used as seeds for crystallization. The mole ratios of the reaction mixture are 1.0 SiO_2 : 0.5 TEAOH: 1.9 urea: 1.0 choline chloride: 1.0 NH_4F : 6.4 H_2O . The reaction time ranged from 10-14 days. 1.1 g of zeolite Beta was obtained when the reaction was complete.

Synthesis of ZSM-11 (MEL)

The preparation is similar to the procedures described above for the synthesis of Silicalite-1. The SDA, DPHMII, was prepared according to the method reported by

Fecant and Bais.¹⁷ The other SDA, DECDMPI was synthesized according to the procedure of Nakagawa.¹⁸ The crystallization was carried out at 140 °C and no seeds were added when DPHMII was used as SDA. However, 5% of calcined siliceous ZSM-11 were used for seeding when SDA is DECDMPI. The mole ratios of the starting materials were 1.0 SiO₂: 0.08 organic SDA (DPHMII or DECDMPI): 1.9 urea: 1.0 choline chloride: 1.6 NH₄F: 5.0 H₂O. Phase-pure MEL was formed after 24 days. 0.8 g and 1.0 g of ZSM-11 were produced when DPHMII and DECDMPI were used as the SDA, respectively.

Synthesis of ZSM-39 (MTN)

The preparation is similar to those in the synthesis of Silicalite-1. The SDA used in this case was tetramethylammonium chloride (97%, Sigma-Aldrich). The mole ratios of the starting materials were 1.0 SiO₂: 1.0 TMACl: 1.9 urea: 1.0 choline chloride: 1.0 NH₄F: 5.0 H₂O. The reaction time was 14 days at a temperature of 170 °C. 1.0 g of ZSM-39 was produced when the reaction was completed.

Isolation of Product

The product was obtained by filtration after being washed three times with deionized water. The filtered solid was then washed 5 times with methanol ($\geq 98\%$, CALEDON) and 3 more times with deionized water again. The product was dried in an oven at 100 °C for 24 hours.

Characterization

The powder X-ray (PXRD) patterns of the products were collected on a Rigaku powder diffractometer with Co-K α radiation ($\lambda = 1.79 \text{ \AA}$). The data were collected from 5° to 65° of 2 θ values. The SEM images were obtained by using a LEO (ZEISS) 1530 Field Emission Microscope.

The solid-state NMR spectra were recorded on an Infinity Plus 400 wide-bore magnet spectrometer operating at the field strength of 9.4 T. The magic-angle of 54.7° was carefully set by the ⁷⁹Br signal from KBr. ¹H-¹³C cross polarization (CP), ²⁹Si, ²⁷Al, and

^{19}F magic-angle spinning (MAS) NMR spectra were obtained for selected samples. The ^1H , ^{29}Si , ^{27}Al , ^{19}F and ^{13}C Larmor frequencies of the spectrometer are 399.5, 79.4, 104.1, 375.9, and 100.5 MHz, respectively. ^{29}Si one-pulse MAS and CP MAS spectra were performed using a 7.5 mm HXY probe. The chemical shifts for the ^{29}Si spectra were referenced to the standard tetramethylsilane (TMS, $\delta = 0$ ppm) by using tetrakis(trimethylsilyl)silane (TTMSS) as the secondary standard. TTMSS has two peaks: one at -9.8 ppm and the other at -125.2 ppm. The -9.8 ppm signal was used as the reference peak. The spinning rate was 4.0 kHz. The pulse angle was 30° and the pulse delay was 30 s. ^{27}Al MAS spectra were collected by using a 5.0 mm HFX probe with a spinning rate of 8 kHz. A pulse angle of 30° and a pulse delay of 1 s were used. The ^{27}Al NMR chemical shifts were referenced to 1 M $\text{Al}(\text{NO}_3)_3$ aqueous solution (0 ppm). ^{19}F MAS NMR was carried out using the 4.0 mm HXY probe with a pulse angle of 30° and a pulse delay of 10 s. The ^{19}F shifts were referenced to CFCl_3 (0 ppm) by using α, α, α -trifluorotoluene (-63.7 ppm) as the secondary reference. The isotropic peaks in the ^{19}F spectra were determined by spinning the sample at two different speeds. The ^{13}C CP MAS experiments were performed using the 4.0 mm HXY probe. The Hartmann-Hahn condition was determined on adamantane. The spinning speed was 10 kHz. The ^1H 90° pulse length was 4.5 μs for the ^{13}C CP experiments. The contact time was 2 ms, and the pulse delay was 10 s. Adamantane was used as a secondary standard to reference the ^{13}C chemical shifts to TMS (0 ppm). Adamantane has two ^{13}C signals at 28.8 and 38.2 ppm. The reference was set by using the signal at 38.2 ppm.

Results and Discussion

All zeolites prepared in the urea/choline chloride DES are siliceous except that 5% calcined zeolite Beta seeds added to the initial reaction mixture have Al. The seeds have a Si/Al of about 17. For the syntheses of MFI and BEA, 5% calcined seeds were added to the initial reaction mixture to speed up the crystallization process. The reason why the seeds are calcined is to ensure that the observed ^{13}C signals in the ^{13}C MAS spectra of the final products are solely from the SDAs occluded in the frameworks of the final products during the reaction and are not due to the organic molecules present in the seeds. In the present case, the tetraalkylammonium ions in the reaction mixtures indeed directed the

formation of the final frameworks. No Al sources were added, since in the previous study, we found that the addition of Al slows down the reaction of the syntheses of high-silica zeolites. The mineralizing agent used in all four cases was F^- which was added to the reaction mixtures in the form of NH_4F . F^- ion has been shown to be an effective mineralizing agent that gives siliceous zeolites with fewer defects.²⁰

Tetrapropylammonium bromide (TPABr) as SDA for MFI synthesis

Silicalite-1 was synthesized using TPA^+ as the organic SDA. Under current reaction conditions, the crystallization of MFI requires 5% seeds. The presence of seeds in the reaction mixture provided greater surface areas for the solutes to integrate into the solid phase, therefore enhancing the crystallization rate.²¹ Figure 2a shows the powder X-ray diffraction (PXRD) pattern of the as-synthesized sample, which indicates that the product is phase-pure and is of high crystallinity. The structure of as-made TPA-MFI is orthorhombic and has 12 crystallographically distinct tetrahedral ($T = Si$) sites. However, the ^{29}Si MAS spectrum (Figure 3a) shows several overlapping Q^4 (Si atoms bonded to four other Si atoms through oxygen) peaks. The reason why the individual T-sites were not fully resolved is that the local environments of these chemically equivalent, but crystallographically non-equivalent T sites are very similar. Nonetheless, the ^{29}Si MAS spectrum looks very similar to those of the Silicalite-1 samples prepared by hydrothermal method in the literature.²²

The seeds used were calcined Silicalite-1 sample and any ^{13}C signals observed in the ^{13}C NMR spectra are solely due to the organic SDA added to the initial reaction mixture and NOT from the seeds. The ^{13}C CP MAS spectrum of the product (Figure 4a) clearly indicates that the TPA^+ is indeed present inside the MFI framework. It is interesting to note that there are two different methyl signals at 10.2 and 11.2 ppm. This is because two of the four propyl chains are in the straight channels while the other two are in the sinusoidal channels.²³ The ^{13}C MAS spectrum also indicates the presence of fluoride in the zeolite framework due to the presence of two signals (65.3 and 65.5 ppm) in the lower field. This is due to that in the as-synthesized Silicalite-1, the fluoride is much closer to

the three α -carbon atoms (carbon directly bonded to nitrogen atom of TPA⁺) than the fourth one.²³

Unlike the as-synthesized F-MFI (fluoride MFI) prepared hydrothermally, there are two signals in the ¹⁹F MAS spectrum aside from the small peak -122.8 ppm (Figure 5a). The weak signal at -122.8 ppm indicates the presence of a small amount of SiF₆²⁻, which is an impurity that is often present in the final product of the zeolite synthesis. The chemical shift for SiF₆²⁻ has been reported in several studies and usually falls in the range of -120 to -130 ppm.²⁴⁻²⁶ According to a previous study, the resonance at -68.5 ppm corresponds to the fluoride that is covalently bonded to Si(9) of the ZSM-5 framework.²⁷ There is also a weak signal at -78.6 ppm, which is not usually seen in the high-temperature hydrothermally synthesized F-MFI. Similar situation has been reported in the dense-gel synthesis of F-MFI and F-MEL (fluoride MEL).²⁸⁻²⁹ The presence of this second site is likely due to a non-equivalent fluoride that is covalently bonded to another Si atom in the framework.

The SEM images show that the crystals aggregate together to form a large cluster (Figure 6a). At a higher magnification, we can see that the morphology of the crystal is characteristic of orthorhombic crystal system and the crystal is intergrown. The surface of the crystal is rough, and adhered by small particles (Figure 6b).

Tetraethylammonium hydroxide (TEAOH) as SDA for zeolite Beta

The synthesis of zeolite Beta, which is a high-silica zeolite having 12-membered ring channels and consisted of the intergrowths of two or more polymorphs, also requires the addition of seeds in the initial reaction mixture for the product to be formed.³⁰ Without seeding, MFI becomes the competing phase during crystallization. This is not surprising since TEA⁺ can also act as a SDA for MFI in hydrothermal synthesis.³¹ The BEA seeds used for the reactions were calcined at 500 °C, so any signals observed in the ¹³C MAS spectrum of the final product are not due to the SDA molecules present in the seeds. The PXRD pattern of the as-synthesized sample is shown in Figure 2b; similar to the hydrothermal synthesis of BEA, the resulting product of the reaction is consisted of a mixture of the different polymorphs. The ²⁹Si MAS spectrum of the as-synthesized

sample (Figure 3b) shows at least five signals that are due to the Q^4 Si atoms and a very weak and broad envelop of Q^3 Si atoms that are bonded to one Al through oxygen are in the range of -108.3 to -116 ppm, while the Q^3 SiOH sites are represented by the broad peak at -104.0 ppm.³²⁻³³ The Al present in the seeds ($Si/Al > 17$) is the sole source of Al for the reaction. However, the exact percentage of Al in the as-made sample is too low to be detected by X-ray fluorescence (XRF), indicating the amount of Al is very small. ^{27}Al MAS NMR is extremely sensitive and therefore was used to detect Al species. The spectrum of the as-made final product does show two resonances (Figure S1a). The signal at 55 ppm represents tetrahedral Al in the BEA framework, while the signal close to 0 ppm represents extra-framework octahedral Al species.

The ^{13}C MAS NMR (Figure 4b) shows the presence of TEA^+ ions inside the channels of BEA. The chemical shift at 6.7 ppm corresponds to the methyl carbons, while the one at 52.3 ppm correspond to the methylene carbons that are directly bonded to the nitrogen. ^{19}F MAS spectrum of the as-synthesized sample contains two signals at -58.0 and -70.3 ppm (Figure 5b). The results agree with the as-made TEA-BEA prepared hydrothermally.²⁴ The presence of these two signals means that there are two different F⁻ anions that are covalently bonded to Si atoms in the framework.²⁴ It has been proposed that the fluoride anions are located inside the $[4^35^4]$ cage of the framework (Figure S2).²⁴ The zeolite BEA synthesized under our conditions has relatively small crystal sizes as shown in the SEM images (Figures 6c-d). Under higher magnification, we can see that the F-BEA made under our conditions shows the truncated squared pyramidal shape of the highly faulted BEA structure.

PXRD pattern of the sample calcined at 500 °C shows that the calcined BEA remains highly crystalline upon calcination (Figure 2c). ^{29}Si MAS spectrum of calcined sample, however, exhibits some noticeable changes. Instead of the broad overlapping signals seen in the as-synthesized material, the ^{29}Si MAS spectrum now shows very well resolved sharp peaks, indicating that calcination drastically enhances the local ordering around Si sites. It is well known that calcination can remove the defects in zeolite structure and thus enhance the local ordering around T sites.³⁴ The expanded ^{29}Si MAS spectrum of calcined sample shows nine crystallographically nonequivalent T-sites within the

framework of BEA, which is similar to the highly siliceous dealuminated BEA prepared in hydrothermal conditions (Figure 3c).³² The ^{29}Si MAS spectrum of the calcined sample does not show a signal at -104.0 ppm due to the $-\text{SiOH}$ groups present in the as-synthesized materials, suggesting that calcining the sample “heals” the defects. There is a very weak signal at -108.2 ppm, which can be due to the Q^3 Si sites containing Si atoms connected to one Al and three other Si atoms via oxygen. Compared with the as-synthesized BEA, the calcined sample contains less framework-Al. The peak responsible for the octahedral Al site ($\sim$ -11 ppm) in the ^{27}Al MAS spectrum has a higher intensity than the one for the tetrahedral Al at 55.1 ppm (Figure S1b). It seems that upon calcination, some of the tetrahedral framework Al originating from the seeds popped out of the framework and were converted into octahedral extra-framework Al.³⁴ Reduced Al in the framework of calcined BEA indicated by the ^{27}Al MAS NMR also contributes to the enhanced resolution in ^{29}Si MAS spectrum of calcined BEA.

Tetramethylammonium chloride (TMACl) as the SDA for the syntheses of MTN

When the organic SDA was changed to TMACl, ZSM-39 was produced after 2 weeks of reaction at 170 °C. The PXRD pattern (Figure 2d) of this product is consistent with cubic structure and the sharpness of the reflections indicates high crystallinity. The ^{29}Si MAS spectrum displays three signals at -109.2, -114.1, and -117.3 ppm with a relative intensity ratio of 1: 4: 12, corresponding to the three nonequivalent tetrahedral Si sites in the cubic framework (Figure 3d).³⁵⁻³⁷ Although TMA^+ is known to be one of the organic SDA for MTN type zeolites, the ^{13}C CP MAS NMR spectrum (Figure 4c) reveals that during the course of the reaction, some of the TMA^+ molecules have decomposed into trimethylammonium ions (46.4 ppm).³⁸⁻³⁹ Only a smaller signal at 57.1 ppm is actually from TMA^+ ions. MTN framework contains two different cages and previous work showed that organic species reside in the larger cage with a diameter of 7.5 Å.⁴⁰ The ^{19}F NMR spectrum shows a major signal at -123 ppm, which is assigned to fluoride ions acting as the counter ions for the organic cations (Figure 5c). There is also a very weak

signal at -126.7 ppm that is due to the SiF_6^{2-} impurity.²⁴⁻²⁶ The small peak at -81.1 ppm is assigned to F^- inside the framework. SEM images show the crystals often aggregate together (Figure 6e).

N, N-dipropylhexamethyleneimminium iodide (DPHMII) and *N, N*-diethyl-3, 5-dimethylpiperidinium iodide (DECDMPI) as SDAs for the synthesis of MEL

A zeolite closely related to the MFI structure is ZSM-11 with MEL topology. ZSM-11 has two intersecting 10-ring channel systems, both of which are straight. ZSM-5, on the other hand, also has two intersecting channels. However, one channel is straight and the other is zigzag.⁴¹ The similarity and subtle difference in topology result from the fact that although the pentasil unit is the basic subunits in both zeolites, the corrugated sheets of pentasil chains are related by a mirror plane in MEL, whereas in MFI, the sheets of pentasil chains are related by an inversion center. One of the challenges in preparing phase pure MEL zeolite is to avoid the intergrowth of MFI in the product.

The organic SDA used in the present experiment is DPHMII. Our results indicate that under the conditions employed, temperature has profound effect on MEL synthesis. When crystallization was carried out at 170 °C for 3 weeks, pure ZSM-39 with MTN topology was produced rather than desired MEL as shown by the PXRD pattern (Figure 2e). The formation of MTN is also confirmed by the ^{29}Si MAS spectrum (Figure 3e) which shows three crystallographically distinct T-sites expected from ZSM-39. There may be two reasons that account for the formation of MTN. First, dense frameworks are usually the preferred products at higher temperatures. Secondly, the reaction time under ionothermal conditions tends to be longer than that in hydrothermal synthesis. This is because in ionothermal synthesis, the lack of water results in poor solubility of reactants and slow transportation of reactive species. Furthermore, the SDA, DPHMII appears to be decomposed at 170 °C over the course of the reaction. The ^{13}C CP MAS (Figure 4d) shows that the organic species occluded inside the pores of the final product is the trimethylammonium ion, which was also observed in the MTN synthesized using TMACl.³⁸ The trimethylammonium ions found inside the framework apparently come

from the decomposition of DPHMII during the reaction. The ^{19}F MAS spectrum (Figure 5d) of this sample has a strong peak at -123.1 ppm, corresponding to the F^- ions that are not covalently bonded to Si. This observation suggests that vast majority of the fluorides act as the charge balancing anion for the organic SDA cations. There is also a small amount of SiF_6^{2-} as indicated by the weak signal at -127.1 ppm.²⁴⁻²⁶ The lack of F^- peak in the region at -60 to -80 ppm suggests that no fluoride ions are covalently bound to framework Si. This observation indicates that the formation of MTN under current conditions largely results from the high reaction temperature, rather than from the structure-directing effect of the F^- .

The SEM images show that the sample contains both single and inter-grown crystals (Figure 6g). As mentioned earlier, the MTN samples prepared by using TMA^+ as SDA in urea/choline chloride mixture exhibits dodecahedral morphology, whereas the MTN crystals obtained from the same DES but containing DPHMII in the starting material are perfect octahedral (Figure 6h). Such morphology has been reported in the non-aqueous synthesis of ZSM-39 in the presence of propylamine and NaOH.²⁴ This octahedral morphology is also very common for solids in the cubic crystal system.⁴² The crystals in this case have much smoother surfaces than the TMA-MTN mentioned earlier. This can be attributed to the longer reaction time, which heals the crystal defects.⁴³ It seems that when using urea/choline chloride DES, the morphology of MTN zeolites can be controlled by choosing different SDAs.

To avoid the formation of dense frameworks, a lower temperature must be used for the preparation of MEL. Indeed, when the temperature was lowered to 140 °C, phase-pure MEL free of any MFI intergrowths was produced as indicated by the weak reflection at $2\theta = 21.8^\circ$ and a strong single peak reflection at $2\theta = 53.1^\circ$ in the PXRD pattern (Figure 2f).⁴⁴ The sample contains long needles clumped together shown by the SEM images (Figure 6i). At higher magnification (Figure 6j), each end of the needle contains a pyramid. This morphology is typical for ZSM-11.

The ^{29}Si MAS spectrum in Figure 3f shows that the sample contains a small amount of Q^3 Si atoms, indicating the presence of defects in the final product. The fully condensed Q^4

signal is considerably larger than that of the Q^3 . The broad peak for Q^4 Si atoms results from overlapping of seven crystallographically non-equivalent Si sites in the crystal lattice.⁴⁵ The ^{13}C CP MAS spectrum (Figure 4e) reveals the presence of DPHMII inside the as-synthesized framework structure. There are six different carbon environments in total, where the signals from the two methylene carbons (one from the propyl chain and the other from the hexamethyleneiminium ring) directly bound to the nitrogen overlap, giving rise to a broad peak (see Figure S4 for carbon numbering). The ionothermal preparation of MEL using DPHMII without seeding is highly reproducible, which suggests the strong structure-directing ability of this particular organic SDA. The ^{19}F MAS spectrum (Figure 5e) contains two major peaks at -65.3 and -77.6 ppm similar to the case observed in MFI. As mentioned earlier, the peaks in the range -60 to -80 are normally due to the fluoride ions that are covalently bonded to the framework Si. ^{19}F NMR results indicate strong interactions between F^- and Si, which suggests that F^- may also play a role in the formation of MEL structure. The fact that both peaks in Figure 5e are fairly broad suggests that the F^- ions may be bound to the Si atoms randomly, rather than specific sites. There is a small amount of SiF_6^{2-} as indicated by the shift at -123.4 ppm.²⁴⁻²⁶

DECDMPI (Figure 1b) was also used as SDA to produce ZSM-11 in the same DES. This molecule is known to have the ability of producing phase-pure MEL under hydrothermal and dense gel conditions.^{18,29} Since we were interested in the effect of different SDAs on crystallization of ZSM-11 in the DES of urea/choline chloride, DPHMII was replaced with DECDMPI. The organic SDA: SiO_2 ratio remained at 0.08: 1, and the temperature of the reaction was also kept the same at 140 °C. 5% of calcined MEL seeds were added to the initial mixture.

Figure 2g shows the PXRD pattern of the as-made product, which clearly indicates that the product obtained after 24 days is ZSM-11. It is phase-pure and free of any MFI intergrowths as indicated by the weak reflection at $2\theta = 21.8^\circ$ and a strong single peak reflection at $2\theta = 53.1^\circ$.⁴³ The ^{29}Si MAS spectrum shows a Q^4 region with severe overlapping peaks due to the seven T-sites (Figure 3g).⁴⁵ Like the DPHMII-MEL, there is also a very small amount of Q^3 Si atoms, meaning that the framework contains some

defects. The ^{13}C CP MAS (Figure 4f) shows that DECDMP⁺ is intact and occluded inside the framework. The spectrum also indicates that two ethyl groups attached to the nitrogen of the piperidinium ring are not equivalent, since one ethyl group is at the equatorial, while the other is at the axial position. The chemical shifts for the carbons of the equatorial groups appear in the lower field, because they are more deshielded than the ethyl groups occupying the axial position (see Figure S4 for carbon numbering). The ^{19}F MAS spectrum (Figure 5f) for the as-made DECDMP-MEL is similar to what has been observed in the DPHMI-MEL case, where there are two major peaks. The signal corresponding to the fluorides that forms a covalent bond with Si is at -67.7 and -77.7 ppm. The weak resonance at -128.6 ppm represents the SiF_6^{2-} impurity.²⁴⁻²⁶

The SEM images (Figures 6k, 6l) of the as-synthesized sample show that the crystals of ZSM-11 are also long needles. Furthermore, there is a greater size distribution in this case: Some crystals are larger than the others (Figure 6k), which is probably due to the use of seeds. During crystallization, crystal growth can occur on the surfaces of the seeds. Some of the seeds might have been dissolved into smaller pieces, which can also provide sites for the amorphous silica to adhere.

The crystallization process involving DECDMPI as the organic SDA was much slower if no seeds were added to the initial stage (Figure S3). Without seeding, crystallization only started after 24 day, while the reaction was already finished when 5% of the seeds were used. The addition of seeds speeds up the reaction by providing a greater surface area for the solutes to integrate into the solid phase.²¹ The choice of organic SDA for MEL zeolite has been shown to be important in both hydrothermal and low temperature dense gel syntheses.²⁹ The requirement of seeding for MEL preparation using DECDMPI as SDA was reported before. For example, the fluoride synthesis of ZSM-11 using DECDMPI as the organic SDA in the dense gel must be initiated by seeding.²⁹ Comparing this result with what we had for the DPHMII discussed previously, we can conclude that the DECDMPI's structure-directing ability toward the MEL type framework is much weaker than that of DPHMII.

Conclusion

In conclusion, our results present the first example of high-silica and siliceous zeolite synthesis in the urea/choline chloride mixture using F^- as the mineralizing agent. We have shown that by using different organic SDA, several types of framework structures can be achieved. The zeolites obtained under the described conditions are all phase-pure, and the results exhibit high reproducibility. Upon calcination, zeolite Beta synthesized in urea/choline chloride has very high crystallinity as shown in ^{29}Si MAS NMR spectrum. The synthesis of ZSM-11 has been challenging due to the intergrown structure formed with ZSM-5. The synthesis of phase-pure ZSM-11 using eutectic solvents or ionic liquid has not been reported in any literatures. With our results of ZSM-11 preparation, both DPHMII and DECDMPI generate phase-pure MEL free of any MFI intergrowths. However, the choice of organic SDA is critical to our reaction conditions as it is in the hydrothermal and dense gel syntheses. The DPHMII molecule has a much stronger structure-directing power toward the MEL framework in the urea/choline chloride mixture, allowing the reaction to proceed without the addition of calcined seeds. For MTN zeolite, morphology may be controlled in the urea/choline chloride by choosing different SDAs. The disadvantage of this system is the long reaction times compared to those in the hydrothermal conditions. Also, some framework structures require the addition of seeds to the initiation of the reaction or the shortening of the crystallization time.

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Figures

(a)

(b)

Figure 1. Organic SDAs used for syntheses of ZSM-11: (a) *N,N*-dipropylhexamethyleneiminium iodide (DPHMII), and (b) *N,N*-diethyl-3,5-dimethylpiperidinium iodide (DECDMPI)

Figure 2. PXRD patterns of as-synthesized (A.S.) (a) MFI, (b) BEA, (c) calcined BEA, (d) MTN from TMA^+ , (e) MTN from DPHMII, and (f) MEL from DPHMII, (g) MEL from DECDMPI.

Figure 3. ^{29}Si MAS spectra of as-synthesized (a) MFI, (b) BEA, (c) calcined BEA, (d) MTN from TMACl, (e) MTN from DPHMII, (f) MEL from DPHMII, and (g) MEL from DECDMPI.

Figure 4. ^{13}C CP MAS spectra of as-synthesized (a) MFI, (b) BEA, (c) MTN from TMACl, (d) MTN from DPHMII, (e) MEL prepared using DPHMII as the organic SDA, and (f) MEL prepared using DECDMPI as the organic SDA. The numbers for (e) and (f) indicates peak assignments (see Figure S4).

Figure 5. ^{19}F MAS spectra of as-synthesized (a) MFI, (b) BEA, (c) MTN from TMACl, (d) MTN from DPHMII, (e) MEL prepared using DPHMII as the organic SDA, and (f) MEL prepared using DECDMPI as the organic SDA. The spinning side bands are indicated by “*” and “o”.

Figure 6. SEM images showing: (a) an overview and (b) a single crystal of the as-made Silicalite-1; (c) an overview and (d) expanded view of as-synthesized BEA; (e) an overview and (f) expanded view of as-synthesized TMA-MTN; (g) an overview and (h) expanded view of as-synthesized MTN from a reaction mixture containing DPHMII at

170 °C; (i) an overview and (j) expanded view of as-synthesized DPHMI-MEL; (k) an overview and (l) expanded view of as-synthesized DECDMP-MEL.

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