A Dynamic Organic Structuring-Directing Agent for Pure-Silica-Zeolite AST and LTA Syntheses

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Abstract: Pure-silica-zeolite (PSZ) AST and LTA are synthesized successfully by using the same structure-directing agent (SDA) molecule, but at different concentrations. A dynamic organic SDA is proposed to discuss the mechanism of phase discrimination between AST and LTA. Data suggest that the SDA molecules can self-assemble into dimer or trimer complexes at different concentrations by π - π interactions, and these differences can be taken advantage of to selectively synthesize either PSZ AST or LTA. These deviations from the Liebau's rules indicate that small changes in SDA chemistry, structure, and order in solution can have a great impact on the structure selectivity of the zeolite synthesis.

Key words: zeolite; synthesis; dynamic structure-directing agent; π - π conjugation; Liebau's rules

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Zeolites comprise a unique class of industrially significant materials. Their broad impact is due in large part to their uniform and tunable physicochemical properties, such as their composition, pore size, and pore topology [1]. Additionally, zeolites have high surface areas, the ability to sieve molecules based on their size and shape, and internal surface chemistries that can range from acidic to basic and hydrophobic to hydrophilic [2]. These exceptional combinations of tunable properties make zeolites excellent candidates for petroleum refining and petrochemical processing applications as catalysts, adsorption and separation materials, and ion exchangers [1,3–6]. To date, 191 zeolite frameworks have been recognized and assigned with the three-letter framework codes by the International Zeolite Association [7]. Many more topologies, with an enormous variety of microporous void shapes, have been predicted, although their synthesis has yet to be demonstrated [8,9]. Typically, zeolites can be synthesized in a large number of aluminosilicate compositions; however, the high-silica (Si/Al > 5) and pure-silica zeolite compositions are often of primary interest for many of the aforementioned applications due to their high hydrothermal stability, acid catalytic activity, and hydrophobicity [10]. Because the production of a zeolite with the appropriate combination of structure and composition for a selected application can be a complex process, the use of organic structure-directing agents (SDAs) to help guide the formation of a particular structure

can be very beneficial [11–14]. For instance, the proper selection and application of an SDA can help discriminate energetically between two closely related structures that strongly compete during synthesis, such as the ISV/BEC topologies and the SSZ-70 series [15–19]. This discrimination behavior can be attributed to the SDA's structure, composition, or interactions with the zeolite precursor gel. However, in many cases (such as ITQ-7 [20] and polymorph C of zeolite Beta [21,22]), SDAs with the correct features have not yet been found. Therefore, exploring the range of existing organic SDAs in terms of the solution chemistry, structure, and composition is of particular interest for the development of high-purity, high- and pure-silica zeolite structures for a variety of applications.

The ability of a molecule to act in a structure-directing role is determined in large part by its hydrophobicity, or ability to transfer between organic and aqueous phases in a zeolite precursor gel. Quaternary ammonium molecules with a moderate hydrophobicity (a C/N⁺ ratio of 11–16) tend to direct the formation of high-silica zeolites [12,17,23]. In general, the Liebau's rules that describe conditions at which organic guest molecules best form clathrasils can be used as guidelines for the selection of molecules appropriate for use as structure-directing agents [24]. First, there must be sufficient room within a particular cage or pore for the molecule. Second, the molecule must be stable under the synthesis conditions. Third, the molecule should

fit within the inner surface of the cage with as many van der Waals contacts as possible, but with the least deformation. Fourth, the molecule should have only a weak tendency to form complexes with the solvent, and maintain an appropriate balance between hydrophobicity and hydrophilicity. Fifth and finally, molecules that are rigid will tend to form clathrasils more easily than flexible molecules, and their ability to do so will increase with increasing basicity or polarizability.

In order to develop an organic SDA that can easily discriminate between similar and competitive zeolite structures, the molecule must first be evaluated for its structure-directing ability. This is most easily accomplished by selecting an SDA with known structure-directing abilities, and modifying said ability in such a way that its interactions with the zeolite precursor gel are adjusted, by changes in structure, composition, or other physicochemical properties. In this paper, we study a dynamic organic SDA for zeolite synthesis, which can self-assemble to form a series of oligomers at different concentrations by π - π conjugation. This SDA has been reported to synthesize pure-silica, as well as Al-free, LTA at specific solution concentrations [25]. LTA is one of the most important synthetic zeolites for industrial applications, and is widely used for molecular separations and detergents [3]. Additionally, pure-silica LTA shows potential for gas separations in the presence of polar molecules such as water, while high-silica LTA is highly selective for olefin cracking, which is important in fluid catalytic cracking operations [25]. Moreover, pure-silica LTA may be an interesting material for low dielectric constant applications [26,27]. Here, we report the ability of the organic SDA for pure-silica LTA to also guide in the production of pure-silica AST, a typical clathrasil-based zeolite, which contains pores and cages of 0-dimension [12]. The use of this supramolecular self-assembling organic SDA to produce pure-silica AST represents a new facile synthesis method for AST, and provides valuable insights into organic SDA modification for structure discrimination during zeolite synthesis.

1 Experimental

1.1 SDA synthesis

The organic structure-directing agent (ROH) studied here,

Scheme 1. Synthetic organic routine to the SDA ROH (i) quaternization of the julolidine molecule to the ammonium iodide salt, (ii) ion exchange of the salt to the final hydroxide product, ROH.

4-methyl-2,3,6,7-tetrahydro-1*H*,5*H*-pirido[3,2-*ij*]-quinolinium, was synthesized via modifications to literature protocols designed by Katayama et al. [28] (Scheme 1). Specifically, 12.017 g julolidine (Acros) was dissolved in 100 mL chloroform (EMD), to which was added 11.5 mL filtered methyl iodide (Aldrich). The reaction mixture was then stirred at room temperature under nitrogen protection. After three and six days of stirring, respectively, the addition of the same amount of methyl iodide was repeated, followed by three more days of stirring. Nine days of reaction time was found to be sufficient for the full quaternization of the amine, and the solution was then quenched with 50 mL cold methanol. The crude product, a red solid, was collected by filtration, and then washed exhaustively with ether and vacuum dried. Recrystallization of the crude product was carried out by first dissolving it in 100 mL dichloromethane (EMD) at the boiling point of the solvent before adding 50 mL of hexane (EMD) down the sides of the flask. Afterward, the whole flask was covered with parafilm and placed in a freezer overnight. The crystals were collected by filtration and washed with 100 mL of cold hexane. The recrystallization procedure was repeated to obtain a high-purity, light yellow powder. The product, an ammonium iodide salt, was ion-exchanged to its active hydroxide form. The salt was dissolved in 375 mL deionized water, followed by adding 35 g Bio-Rad AGI-X8 (Bio-Rad) ion exchange resin, and stirring for 24 h at room temperature. The mixture was then filtered to remove the resin. The degree of ion-exchange was determined by titration with 0.01 mol/L hydrochloric acid (J.T. Baker). The process was repeated 1–2 times until a 90% or greater conversion was reached. Finally, water was evaporated from the light yellow solution using a rotary evaporator to get the desired concentration, and the final solution was stored in a refrigerator for zeolite synthesis.

1.2 Zeolite synthesis

Both pure-silica LTA and AST were synthesized from precursor gels of the following molar compositions: $\text{SiO}_2:0.25 \text{ ROH}:0.25 \text{ TMAOH}:0.5 \text{ HF}:x \text{ H}_2\text{O}$, where x varied from 2 to 8; a similar method to that employed by Corma et al. [25]. The gel was prepared in a Teflon jar, covered with parafilm, by hydrolyzing tetraethylorthosilicate (TEOS, Aldrich) in an aqueous solution of the structure

directing agent, ROH and tetramethyl-ammonium hydroxide (TMAOH, 25% aqueous solution, Sachem) while stirring for 24 h. Here, the initial concentration of ROH solution was found to be critical for the production of the desired phase. If the concentration was between 0.1 and 0.2 mol/L, the synthesis precursor could produce PSZ LTA. Once the concentration was higher than 0.3 mol/L, the synthesis precursor produced PSZ AST. The reason is believed to be the different structure of ROH molecules in the synthesis solution (refer to results and discussion section). After hydrolysis, the clear solution was evaporated using a vacuum desiccator to remove the unwanted ethanol and water. In some cases, water was added back to the jar, as necessary, to obtain the correct total mass (around 2 g). Finally, an aqueous solution of hydrofluoric acid (48%, Mallinckrodt) was added, and the mixture was stirred with a Teflon spatula. The mixture was introduced into a Teflon-lined Parr autoclave (Bomb 4749, 23 mL) and hydrothermally reacted at 135 °C. After 7–14 d, the reactor was removed from the oven and cooled. The final mixture was sonicated and washed with acetone and water, which was then filtered and dried to obtain the crystalline powder.

1.3 Characterization

The chemical formula of ROH was confirmed by ^{13}C and ^1H nuclear magnetic resonance (NMR) spectroscopy (Varian INOVA 400). The conjugation of ROH molecules in an aqueous solution at different concentrations was studied by UV-Vis absorption spectroscopy (Varian Cary 50 UV/Vis spectrophotometers, 190–1100 nm) and photoluminescence spectroscopy (Spex Fluorolog Tau-3 fluorescence spectrophotometer). The zeolite structures were characterized using powder X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer with Cu K_α radiation) and scanning electron microscopy (SEM, Philips XL30-FEG). The conformation of the SDA in the as-made zeolite crystals was also studied by solid-state photoluminescence spectroscopy (Spex Fluorolog Tau-3 fluorescence spectrophotometer). Lastly, thermogravimetric analysis (TGA) was performed on both

zeolite structures (Mettler Toledo TGA/SDTA851[®]) with a ramp rate of 10 °C/min.

2 Results and discussion

2.1 Structure-directing agent

The structure directing agent, ROH, was successfully synthesized, and was confirmed by ^{13}C -NMR and ^1H -NMR. For instance, ^{13}C -NMR (100 MHz, D_2O , δ) spectrum (Fig. 1(a)) shows peaks at δ of 18.2, 26.0, 52.8, 66.0, 131.0, 131.8, and the corresponding distortionless enhancement by polarization transfer (DEPT) 135 spectrum (Fig. 1(b)) shows peaks at δ of 53.2 (CH_3), 131.2 & 132.0 (CH), 18.1, 26.0 & 66.0 (CH_2). The integration of ^1H -NMR (400 MHz, D_2O , δ) spectrum confirms that the ratio of 1H:2H:3H is 1:4:1, corresponding to a $\text{CH}:\text{CH}_2:\text{CH}_3$ ratio equal to 3:6:1.

Fig. 1. ^{13}C -NMR (a) and the corresponding distortionless enhancement by polarization transfer (DEPT) 135 (b) spectrum of ROH.

It should be noted that the ROH molecule is planar and contains an aromatic ring, which makes it possible to stack these molecules together to form π -bonded complexes, e.g., dimer, trimer, and larger oligomers, as shown in Scheme 2. It is well known that π - π interactions act strongly on flat polycyclic aromatic hydrocarbons such as anthracene, triphenylene, and coronene because of the many delocalized

Scheme 2. Molecular structure of ROH monomer, dimer, and trimer.

π -electrons. In this study, the π - π interaction, which is stronger than other noncovalent interactions, plays an important role in structure direction, which will be discussed later. Here, we found that the π - π stacking behavior begins to dominate when the concentration of ROH in the solution increases. Different degrees of stacking results in variations in the LUMO band energy, which can be observed by UV-Vis absorption and photoluminescence. Figure 2 shows the UV-Vis absorption spectra of the ROH solution at different concentrations. For instance, at a concentration of 0.001 mol/L, the SDA can be considered a monomer in solution, since it showed no absorption between 280 and 400 nm. As the concentration of the ROH increased, the absorption over the entire wavelength spectrum became more intense, and the absorption range was seen to red-shift to a higher wavelength.

Fig. 2. UV-Vis absorption spectra of ROH at different concentrations.

The red-shifting of LUMO band energy could also be observed in photoluminescence spectra of the ROH solutions at different concentrations (Fig. 3(a)). For this technique, the excitation wavelength was 265 nm. It is clear that the ROH molecules were mainly in monomer form at a concentration of 0.001 mol/L, since the ROH monomers

exhibited strong excitations at wavelengths of 310 nm and 620 nm. The shoulder between the wavelengths of 400 and 500 nm indicated that there were small amount of oligomers in the solution. For the 0.01 mol/L ROH solution, monomers were still the dominant species, although dimers or larger oligomers were increasingly present. Once the concentration was higher than 0.10 mol/L, there were no detectable monomers in the solution, suggesting that the majority of ROH molecules were in the form of dimers, trimers, or larger oligomers. The increase in concentration from 0.01 mol/L could also be tracked by the red-shifting of the excitation peak of the dimer form of the molecule from 410 nm (0.01 mol/L) to higher wavelengths (e.g., 440 nm at 0.10 mol/L, 460 nm at 0.20 mol/L, 480 nm at 0.50 mol/L, and 500 nm at 1.00 mol/L). This was also the case for the UV-Vis spectra because the energy of LUMO band for the complex is reduced as the number of π - π interactions increases.

2.2 Zeolite synthesis

After synthesizing pure-silica AST and LTA, the crystal-line structures were identified by the XRD powder pattern as shown in Fig. 4. Pure-silica AST and LTA crystals were synthesized from the same precursor gel molar compositions as mentioned in the experimental section. The only difference between the two precursor gels was the initial concentration of the ROH solution. Pure-silica LTA crystals were produced if the concentration was between 0.1 and 0.2 mol/L, whereas PSZ AST crystals were formed once the concentration was higher than 0.3 mol/L. According to the UV-Vis spectra and photoluminescence spectra, this concentration corresponds to ROH molecules in dimer form and trimer form, respectively, for the LTA and AST precursor gels. In the 24 h of hydrolyzing TEOS, silica species were attracted by the positive, charged center of the R^+ and TMA^+ ions to form a scaffold around the ROH complex and

Fig. 3. Photoluminescence spectra of ROH solution at different concentrations (a) and as-synthesized AST and LTA (b). The excitation wavelength is 265 nm.

Fig. 4. Powder XRD patterns of as-synthesized AST and LTA.

the TMAOH molecules. This was followed by silica condensation around each of the SDA ions with short range interactions. We speculate that due to a higher charge density of the ROH trimer complex, compared to the ROH dimer, the ROH trimer was more capable of interacting closely with the silica precursors, therefore aiding in the formation of the AST structure, whose cage was less open than LTA. Figure 5 shows the crystalline morphology of LTA and AST. LTA has cubic (isometric) morphology, which is completely different from AST, which has bipyramid morphology.

The status of the ROH molecules inside the pores and cages of the as-made zeolite framework was investigated by solid-state photoluminescence spectroscopy, and the results

are shown in Fig. 3(b). In LTA, the ROH molecules were primarily in dimer form, which is excited at 430 nm. This was consistent with the fact that ROH molecules were mostly in dimer form in synthesis precursor for pure-silica LTA formation. Interestingly, there was a noticeable excitation at wavelength of 310 nm, which indicated that there was still small amount of ROH molecules in monomer form. In AST, the spectra confirmed the absence of monomers of ROH within the framework due to the lack of a peak at 310 nm. Instead, the spectra showed a broad excitation plateau from 330 to 570 nm. It was difficult to identify which oligomer species existed in the AST as-synthesized crystals due to a lack of separate, identifiable peaks in this region. However, it is likely that the ROH molecules were in trimer form, which was their status in the synthesis precursor gel. Additionally, the broad plateau could be caused by the deformation of the trimer complex in the confined space in AST crystals, rather than the presence of many different oligomer species.

As shown in Fig. 6, AST and LTA have similar topology. Both are composed of 4–1 secondary building units (SBUs) and contain d4Rs. Further, they both have a large cage structure of similar volume. However, AST crystals contain cages of 4^66^{12} and composite building units of $4^6(\text{d4R})$ at ratio of 1:1, while LTA crystals contain cages of $4^86^88^6$ and composite building units 4^66^8 & 4^6 at a ratio of 1:1:2. This is important because the space in the AST cage is theoretically

Fig. 5. SEM images of as-synthesized pure-silica LTA (a) and AST (b).

Fig. 6. The framework structure of LTA viewed along the [001] axis (a) and AST viewed along the [100] axis (b).

sufficient for the ROH dimer, but slightly crowded for the trimer complex; hence, the trimer complex may be distorted inside the cage. On the other hand, the $4^86^88^6$ cage of the LTA structure has six 8-rings, one on each face, which makes the framework three-dimensional and much more open than the 4^66^{12} cage of AST. Additionally, AST has a framework density (FD, defined as the number of tetrahedral atoms per $1000 \text{ \AA}^3$) of 15.8, higher than LTA (FD of 14.2).

TGA results (Fig. 7) show the weight loss of both as-made LTA and AST powder in air from 80 to 700°C with ramping rate of $10^\circ\text{C}/\text{min}$. After the heating process, as-synthesized AST lost 22.7% weight total, and the crystals turned black, indicating that organic residues were trapped inside the cages. On the other hand, LTA became white after the programmed heating, and the lost weight of 35.2% total, much higher than the 22.7% of the as-made AST powder. The three-dimensional channels, consisting of the 8-ring windows between cages, therefore helped oxygen and degraded gases travel through the framework.

Fig. 7. TGA weight loss results of LTA and AST in air from 80 to 700°C with a temperature ramping rate of $10^\circ\text{C}/\text{min}$.

2.3 Structure-directing mechanisms

Based on the spectroscopic absorption analysis, it appears that the reason AST is formed at higher complexations of the ROH is that the trimer and larger oligomer species have

the ability to attract or interact with more of the silica source in the precursor gel so that the silica precursor species form a cage with small rings instead of large windows (e.g., 4-rings and 6-rings instead of 8-rings or larger ones). It is important to note that the complexation differences were the only difference in the synthetic approach; here, the C/N^+ ratio was maintained at 13 [12,17].

Camblor and colleagues found that a decrease in the $\text{H}_2\text{O}/\text{SiO}_2$ ratio favored the crystallization of the least dense phase frequently if a SDA in fluoride medium permitted the crystallization of several phases. Such a trend was thought to be due to a kinetic effect favoring metastable phases (which are, generally, the less dense phases) at high supersaturations (presumably achieved at low water/silica ratios) [29]. However, the results in this study provide an opposite consequence of a decrease in the $\text{H}_2\text{O}/\text{SiO}_2$ because LTA has lower framework density than AST. Such confliction can be explained by the self-assembly of dynamic SDA.

Although the rules summarized by Gerke, Gies and Liebau can, in some sense, steer the development of our understanding of the relationships between the organic SDAs and the pores or cages of the resulting structure, it should be noted that they are heuristics and are therefore not applicable to all situations [30]. For example, VPI-5 syntheses result in a structure in which the organic molecule is not even present inside the pores of the molecular sieve [31,32]. The case reported here is another example of a gap in our understanding of the principles that drive the relationship between organic guest and structure. First, the cage in AST crystals does not have sufficient room for the ROH trimer, causing the complex to deform inside the cage. The heuristic principles state that the molecule should fit the inner surface of the cage with as many van der Waals contacts as possible, but with the least deformation. In this case, there must be a balance between van der Waals contacts and molecule deformation. Second, the two synthesis precursors started from different concentrations but ended with exactly the same composition. This indicates that the aging process is critical for zeolite synthesis, and the final framework may be determined during this process. These deviations from Liebau's rules indicate that small changes in SDA chemistry, structure, and order in solution can have a great impact on the structure selectivity of the zeolite synthesis. A deeper understanding of the relationship between SDA chemistry, such as those discussed here, and zeolite formation could lead to improvements both in the design of SDA molecules used to search for new zeolite structures and the production of zeolites.

3 Conclusions

In this paper, we report the facile synthesis of both PSZ

LTA and AST using the same SDA molecule and discuss the mechanism by which selectivity is established. The concentration, and therefore the conjugation state, of the dynamic organic structure-directing agent (ROH) for pure-silica LTA is critical for discriminating between the LTA and AST phases during zeolite synthesis. The ROH appears to be able to self-assemble into dimer or trimer complexes at different concentrations by π - π interactions, and this can be taken advantage of to selectively synthesize either pure-silica LTA or AST.

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