Mechanism of Structure Direction in the Synthesis of Pure-Silica Zeolites. 2. Hydrophobic Hydration and Structural Specificity

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Received December 5, 1994. Revised Manuscript Received March 13, 1995[⊗]

Several syntheses of zeolites that employ organic structure-directing agents are investigated via $^1H-^{29}Si$ CP MAS NMR spectroscopy. Inorganic-organic interactions in the tetrapropylammonium- and 1,6-hexanediamine-mediated syntheses of pure-silica ZSM-5 (Si-ZSM-5) are compared; these results are contrasted to those from the 1,6-hexanediamine-mediated synthesis of pure-silica ZSM-48 (Si-ZSM-48), in which the diamine serves as a pore-filling agent. Synthesis gels containing tetramethylammonium, tetraethylammonium, tetrabutylammonium, tetrapentylammonium, and tetraethanolammonium in lieu of tetrapropylammonium are evaluated by $^1H-^{29}Si$ CP MAS NMR to examine the significance of hydrophobic hydration behavior in structure direction. Finally, the effects of sodium, the silica source, and the substitution of D_2O for H_2O on the kinetics of nucleation and crystallization are discussed in terms of their mechanistic implications. A modified mechanism of structure direction in zeolite synthesis is proposed for which the formation of inorganic-organic composite structures is initiated by overlap of the hydrophobic hydration spheres of the inorganic and organic components, with subsequent release of ordered water to establish favorable intermolecular van der Waals interactions.

Introduction

In previous work, a mechanism of structure direction in the tetrapropylammonium-mediated synthesis of pure-silica analogue of zeolite ZSM-5 (Si-ZSM-5) was proposed based on the results of $^1H-^{29}Si$ cross polarization, magic angle spinning (CP MAS) NMR.[1,2] The NMR data suggested that upon heating of the synthesis gel, close contact between the protons of tetrapropylammonium (TPA) and the silicon atoms of the inorganic phase, i.e., on the order of van der Waals interactions,[3] is established prior to the formation of the long-range order of the crystalline zeolite structure. It was proposed that silicate is closely associated with the TPA molecules, thus forming inorganic-organic composite species that are the key species in the nucleation and crystal growth processes for the self-assembly of Si-ZSM-5. This description of inorganic-organic interactions in structure direction leads to questions regarding the nature of these interactions and how an understanding thereof can be applied to the design and synthesis of novel zeolite pore architectures. One of the primary issues is how these intermolecular interactions give rise to a particular zeolite structure, i.e., the origin of structural specificity. Additionally, the extent to which the occurrence of the cross-polarization phenomenon in a sample that appears amorphous by X-ray powder diffraction can be correlated with the occurrence of a structure-directing effect remains to be clarified.

A comparison of the cross polarization profiles from syntheses using two different structure-directing agents that produce the same zeolite structure should provide relevant information regarding the features of the organic species and their interactions with the inorganic components that are essential to the phenomenon of structure direction.[4] Similarly, a comparison of the cross-polarization profiles from the syntheses of two different pure-silica zeolites that are formed using the same organic species at different synthesis temperatures should provide insight into the characteristics of the intermolecular interactions that give rise to structural specificity.[4] Appropriate systems in which to examine such influences are the synthesis of Si-ZSM-5 (a structure composed of intersecting 10-ring channels) in the presence of tetrapropylammonium (TPA) and 1,6-hexanediamine (HXN) and the hexanediamine-mediated synthesis of pure-silica ZSM-48 (Si-ZSM-48, a linear 10-ring channel system) at a higher temperature.[5]

The first step in the mechanism proposed for structure direction and self-assembly in the synthesis of Si-ZSM-5 involves the formation of an ordered, hydrophobic hydration sphere around the TPA cation.[1] The phenomenon of hydrophobic hydration has been invoked to account for the excess molar heat capacities of aqueous solutions of tetraalkylammonium species and other soluble, hydrophobic organic species relative to that of pure water (on the order of 0.1 kcal K^{-1} mol^{-1});[6] at the molecular level, hydrophobic hydration is described as the reorientation or restructuring of water

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1995.

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molecules in the vicinity of the hydrophobic solute in order to accommodate the species while maintaining a fully hydrogen-bonded network of water.[7,8] This is in contrast to the hydrophilic hydration of alkali metal ions, for example, in which ion–dipole interactions provide the primary stabilizing interactions and compensate for the hydrogen bonds that are broken due to the spherically symmetric orientation of water molecules.[9] In the proposed mechanism of zeolite synthesis, replacement of the water molecules in the hydrophobic hydration sphere of the structure-directing agent by silicate species generates the inorganic–organic composite species that serve as the key components in nucleation and crystal growth. These species apparently provide the means by which the geometry of the organic structure-directing agent is translated into the zeolite pore architecture. The question thus arises regarding the relationship between the ability of the organic species to form a hydrophobic hydration sphere and the occurrence of structure direction. Is the formation of a hydrophobic hydration sphere an essential step in the mechanism of structure direction? Alternatively, are the same molecular characteristics that lead to hydrophobic hydration also responsible for favorable interactions between the organic species and the resulting pure-silica zeolite framework, without the hydrophobic hydration sphere being directly involved in the structure forming process? In an examination of these issues, the series of symmetric, short-chain tetraalkylammonium ions, i.e., tetramethylammonium (TMA), tetraethylammonium (TEA), TPA, tetrabutylammonium (TBA), and tetrapentylammonium (TPenA), represents a suitable system for study because of the well-documented hydration behavior of these cations[6,10–13] and their utility in numerous zeolite syntheses.[14] Tetraethanolammonium (TEOA) is also included in this series for study because it is approximately the same size as TPA but does not form a hydrophobic hydration sphere (no excess molar heat capacity is observed for aqueous solutions of TEOA) because the alcohol moieties participate in the hydrogen bonding network of water.[6]

In adapting the syntheses of Si-ZSM-5 and Si-ZSM-48 for investigation by the $^1H-^{29}Si$ CP MAS NMR technique, it was observed that the replacement of H_2O by D_2O in the synthesis mixture necessitated longer synthesis times. An isotope effect of D_2O on zeolite crystallization kinetics has been reported only once previously and was attributed to the slowed rates of O–D (versus O–H) bond cleavage and bond formation in the silicate condensation polymerization of zeolite A.[15] In the present investigation of the role of hydrophobic hydration in structure direction, an understanding of the isotope effect may provide additional mechanistic insight. Because zeolite synthesis is a kinetically controlled phenomenon,[16] the mechanism proposed for this process must be consistent with the observed kinetics. Thus, in the present work, additional factors that influence the kinetics of zeolite formation such as the presence of alkali metal ions[17] and the silica source are investigated for their mechanistic implications.

Experimental Section

Synthesis. The sodium-free synthesis procedure for Si-ZSM-5 in which the only sources of protons are the organic structure-directing agent and its hydroxide counterion was performed as described in part 1 of this work.[2] The gel composition for the synthesis of Si-ZSM-5 using fumed SiO_2 (Cab-O-Sil, Grade M-5) was $0.5TPA_2O{:}10SiO_2{:}380D_2O$. The fluid gel was heated statically at 110 °C and autogenous pressure in Teflon-lined, stainless steel reactors for 15 days. Samples were collected from the unheated gel after 1, 10, and 15 days of heating. The samples were freeze-dried according to the procedure described in part 1 of this work. The freeze-dried samples were handled in a N_2 or Ar atmosphere. Spectral analyses were performed on freeze-dried samples both before and after washing with D_2O to remove nonoccluded organic species and soluble silicate species.

For the hexanediamine-mediated syntheses of Si-ZSM-5 and Si-ZSM-48, the gel composition was $5HXN{:}2SiO_2{:}10D_2O$.[5] In a typical synthesis, a gel containing 9.68 g of 1,6-hexanediamine (Aldrich), 2.0 g of fumed SiO_2 (Cab-O-Sil, Grade M-5), and 30.0 g of D_2O was aged for 5 min. The fluid synthesis gel was heated at 120 °C for 60 days to form Si-ZSM-5 or at 150 °C for 15 days to form Si-ZSM-48; when H_2O was used, the synthesis times were 40 and 10 days, respectively. The synthesis temperature of Si-ZSM-5 must be carefully controlled: at 110 °C, no crystalline material is apparent after 60 days of heating, while at 125 °C, some Si-ZSM-48 is crystallized. Samples were collected at intervals by freeze-drying, as described previously.[1,2]

For the experiments involving other tetraalkylammonium (TAA) ions, solutions of approximately 0.5 M TAAOH in D_2O were prepared using Amberlite IRA-400 (OH) anion-exchange resin and TMACl (Aldrich), TEABr (Aldrich), TBABr (Aldrich), or TPenABr (Aldrich) in D_2O; the exact concentrations of TAAOH were determined by titration with 0.096 N HCl. TEOAOH (98%) was used as received from Pfaltz & Bauer. Gels of composition $0.5TAA_2O{:}10SiO_2{:}380D_2O$ were prepared in a manner analogous to the aforementioned synthesis of Si-ZSM-5 using TPAOH. The gels were heated at 110 °C for up to 30 days; a portion of the unheated gel and a sample after 10 days of heating were collected by freeze-drying, whereas the sample at 30 days was collected by cooling to room temperature, filtering, and washing with H_2O. These synthesis gels did not yield any crystalline products after 30 days at 110 °C.

Gels of composition $0.5TAA_2O{:}10\ SiO_2{:}380H_2O$ were also prepared using TEOA or mixtures of TEOA and TPA ($0.29TEOA_2O{:}0.21TPA_2O$ or $0.45TEOA_2O{:}0.05TPA_2O$). These gels were heated at 150 or 175 °C for 7 days. Products were collected by cooling to room temperature, filtering, and washing with H_2O.

For studies of the effect of sodium on the kinetics of Si-ZSM-5 synthesis, gels were prepared with a composition of $0.5TPA_2O{:}3Na_2O{:}380H_2O$ (or D_2O): 10 SiO_2 using $NaNO_3$ (Aldrich) as the sodium source. Investigations of the effect of the silica source involved gels that were prepared with a composition of $0.5TPA_2O{:}380H_2O$ (or D_2O)$:10SiO_2$ using tetraethylorthosilicate (TEOS) as the silica source. For studies of the kinetic effect of deuterated TPA (TPA-d_{28}) on the TPA-mediated synthesis of Si-ZSM-5, gels were prepared with a

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composition of $0.5(TPA\text{-}d_{28})_2O{:}380H_2O$ (or D_2O)$:10SiO_2$ using TEOS as the silica source. $(TPA\text{-}d_{28})Br$ was purchased from Isotec (custom synthesis) and converted to the hydroxide form using Amberlite IRA-400 (OH) anion-exchange resin, as described above. Samples were collected at intervals by cooling to room temperature and drying the entire synthesis mixture under ambient conditions, followed by washing with H_2O and filtering to isolate the solid product.

For kinetic studies of the effect of sodium on the hexanediamine-mediated syntheses of Si-ZSM-5 and Si-ZSM-48, gels were prepared with a composition of $5HXN{:}0.6Na_2O{:}10H_2O$ (or D_2O)$:2\ SiO_2$ using $NaNO_3$ as the sodium source. For seeded syntheses, 5 wt % of the starting silica was replaced by HXN/Si-ZSM-5 (≈85 wt % SiO_2) or HXN/Si-ZSM-48 (≈90 wt % SiO_2), as appropriate. Samples were collected at intervals using the technique described above. HXN/Si-ZSM-5 and HXN/Si-ZSM-48 could not be synthesized using TEOS as the silica source.

Analysis. Solid-state NMR studies were performed on a Bruker AM 300 spectrometer equipped with a Bruker dual-channel MAS probe, a Bruker solid-state CP MAS accessory, and a high-power amplifier, as described in part 1 of this work.[2] Solution-phase NMR was performed using a General Electric QE 300 spectrometer, as described in part 1 of this work.[2]

X-ray powder diffraction (XRD) data were collected on a Scintag XDS-2000 diffractometer using Cu Kα radiation. As a qualitative assessment of the amount of crystalline material present, the percent crystallinity of each sample was determined from the ratio of height of the most intense reflection in the XRD pattern (23.19° 2θ (501) for Si-ZSM-5; 21.3° 2θ for Si-ZSM-48) to the height of the corresponding reflection of the Si-ZSM-5 or Si-ZSM-48 samples prepared using Cab-O-Sil, sodium, and D_2O. Because the choice of reference sample (assigned as 100% crystallinity) is somewhat arbitrary, it is possible that a product may have a percent crystallinity value greater than 100%. For amorphous samples, the percent crystallinity is zero.

IR spectroscopy was performed on a Nicolet System 800 FTIR Instrument. IR samples were prepared as KBr pellets. Thermogravimetric analyses (TGA) were performed on a DuPont 951 thermogravimetric analyzer. Approximately 10 mg of sample was heated at a rate of 5 °C min^{-1} to 600 °C.

Results

Structural Specificity. The XRD, IR, TGA, and $^1H-^{29}Si$ CP MAS NMR data for the crystallization of TPA/Si-ZSM-5 are described in part 1 of this work.[2] In summary, crystalline Si-ZSM-5 is apparent after 5–10 days of heating at 110 °C, and crystallization is complete in 15 days. By TGA, the product has a unit cell composition of $4.6TPA{:}96SiO_2{:}1.5D_2O$. With four channel intersections per unit cell, this equates to approximately one TPA molecule per channel intersection (Figure 1a). Efficient cross polarization between the TPA protons and the silicate species is possible after 1 day of heating[1] even though the material does not exhibit long-range order observable by XRD or IR spectroscopy.[18,19] The efficiency of polarization transfer in the $^1H-^{29}Si$ CP MAS NMR spectrum increases as crystalline TPA/Si-ZSM-5 is formed.

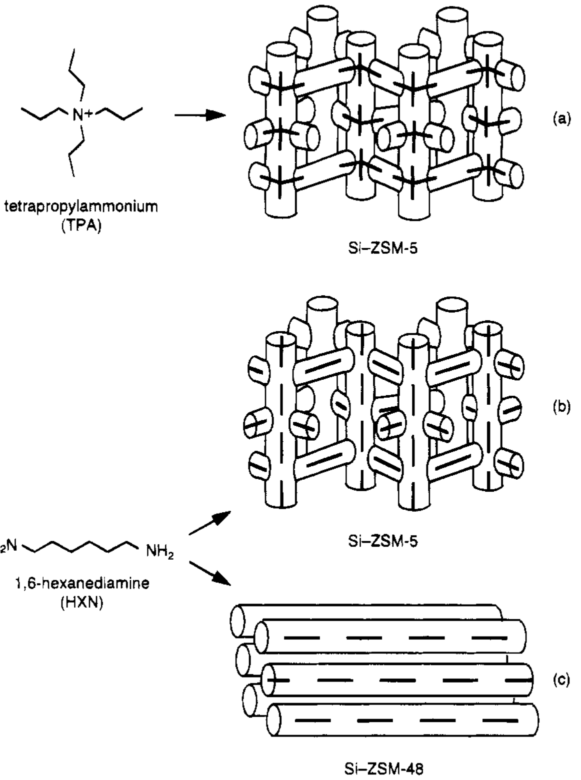

Figure 1. Proposed locations of TPA occluded in Si-ZSM-5 (a), hexanediamine occluded in Si-ZSM-5 (b), and hexanediamine occluded in Si-ZSM-48 (c).

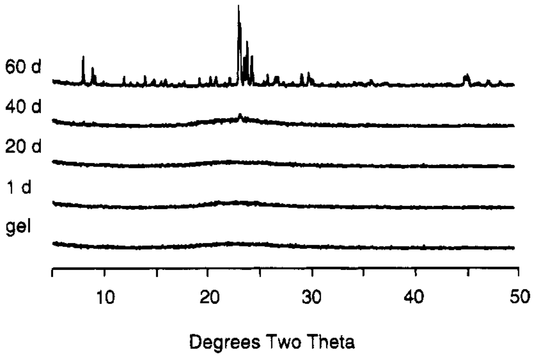

Figure 2. X-ray diffraction patterns of the D_2O-washed, freeze-dried samples collected during the hexanediamine-mediated synthesis of Si-ZSM-5.

The XRD patterns for the washed, freeze-dried samples collected at intervals during the synthesis of HXN/Si-ZSM-5 are shown in Figure 2. Crystalline order observable by XRD (approximately 4–5 unit cells)[18] is present after approximately 30–40 days of heating at 120 °C, and crystallization is complete after 60 days. The IR spectra show that silica ordering that is characteristic of the Si-ZSM-5 structure (band at 550–560 cm^{-1})[18,19] is present after 20 days of heating (Figure 3). TGA of HXN/Si-ZSM-5 indicates two stages of weight loss: the first, from 25 to 305 °C corresponds to desorption of water, and the second, from 305 to 600 °C, corresponds to loss/combustion of hexanediamine. The observed losses of D_2O (2.1 wt %) and diamine (13.6 wt %) indicate a unit cell composition of $8.0HXN{:}96SiO_2{:}7.2\ D_2O$. HXN/Si-ZSM-5 thus contains two hexanediamine molecules per channel intersection, and the organic species completely fill the available void space of the ZSM-5 structure (Figure 1b).

The X-ray powder diffraction data for the washed, freeze-dried samples collected at various time intervals during the synthesis of HXN/Si-ZSM-48 are shown in Figure 4. Some crystalline material is present after 5

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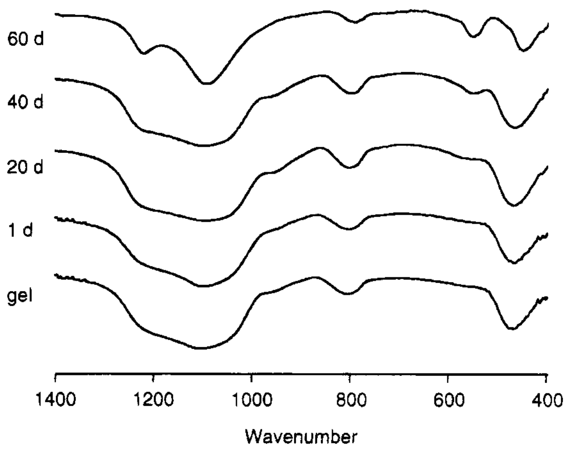

Figure 3. IR spectra of the D_2O-washed, freeze-dried samples collected during the hexanediamine-mediated synthesis of Si-ZSM-5.

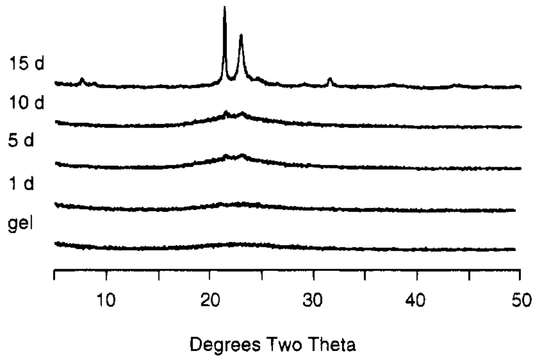

Figure 4. X-ray diffraction patterns of the D_2O-washed, freeze-dried samples collected during the hexanediamine-mediated synthesis of Si-ZSM-48.

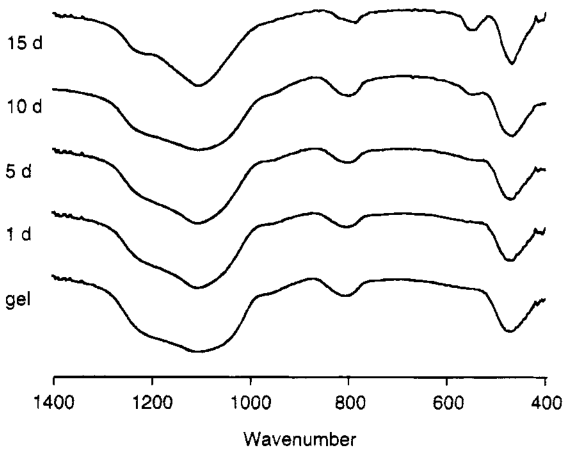

Figure 5. IR spectra of the D_2O-washed, freeze-dried samples collected during the hexanediamine-mediated synthesis of Si-ZSM-48.

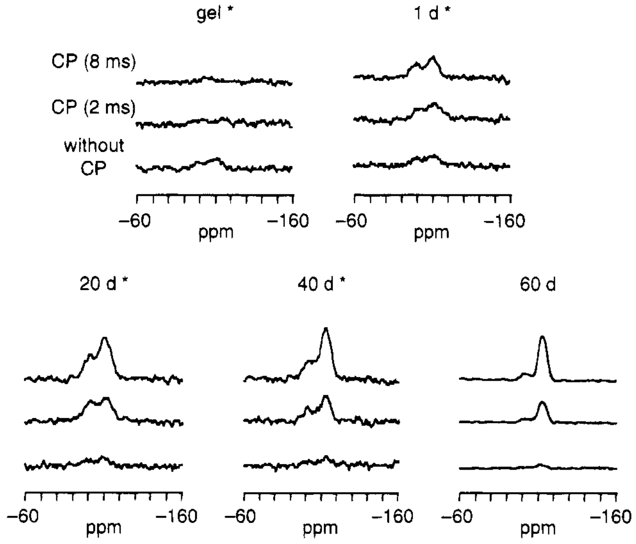

Figure 6. ^{29}Si MAS and $^{1}H-^{29}Si$ CP MAS NMR spectra of the freeze-dried samples collected during the hexanediamine-mediated synthesis of Si-ZSM-5 (CP contact times as indicated; the asterisks indicate an expanded intensity scale (×5)).

days of heating at 150 °C, with crystallization being complete in 15 days. The IR spectra exhibit the same trend in the crystallization profile (Figure 5). TGA of the product shows similar stages of weight loss as HXN/Si-ZSM-5. The observed losses of D_2O (1.8 wt %) and hexanediamine (6.1 wt %) indicate a composition of $3.3HXN{:}96SiO_2{:}5.6D_2O$ (two unit cells).[20] The TGA results indicate that HXN/Si-ZSM-48 has approximately half the organic content of HXN/Si-ZSM-5. However, the void volume of Si-ZSM-48 is also nearly half that of Si-ZSM-5,[21] which implies that hexanediamine completely fills the void space of Si-ZSM-48 (Figure 1c).

The ^{29}Si MAS and $^{1}H-^{29}Si$ CP MAS NMR spectra for the solids collected from the hexanediamine-mediated synthesis of Si-ZSM-5 are shown in Figure 6. As in the spectra from the TPA-mediated synthesis of Si-ZSM-5, two resonances are observed and correspond to Q^3 (downfield resonance) and Q^4 (upfield resonance) species (Q^n represents $Si(OSi)_n(OD)_{4-n}$). During the course of the synthesis, the overall intensities of the spectra obtained without CP remain constant but show an increase in the number of Q^4 sites relative to Q^3. The positions of the Q^3 and Q^4 signals shift from −100 to −102 ppm and from −110 to −112 ppm, respectively, during the transformation from amorphous silica to crystalline Si-ZSM-5; the upfield shift has been correlated with the larger Si−O−Si bond angles present in Si-ZSM-5 versus amorphous silica.[22] Polarization transfer between the protons of hexanediamine and the silicate species does not occur in the unheated gel sample. After the sample has been heated at 120 °C for 1 day, CP between the organic and inorganic components is observed. The intensities of the CP spectra are greater than the intensity of the spectrum obtained without CP, which suggests that polarization transfer is efficient. More efficient polarization transfer is observed in the sample obtained after heating for 20 days even though the solid still does not have long-range order detectable by XRD. Further increases in the intensities of the CP spectra are observed for the partially and completely crystalline samples obtained after 40−60 days of heating. The trend in the efficiency of CP relative to the degree of crystalline order observed by XRD is similar to that observed for the TPA-mediated synthesis of Si-ZSM-5.

The ^{29}Si MAS and $^{1}H-^{29}Si$ CP MAS NMR spectra shown in Figure 7 for the hexanediamine-mediated

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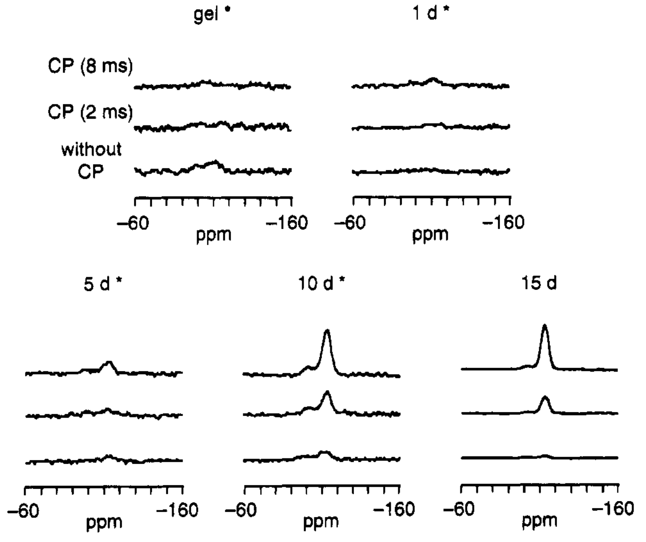

Figure 7. ^{29}Si MAS and $^{1}H-^{29}Si$ CP MAS NMR spectra of the freeze-dried samples collected during the hexanediamine-mediated synthesis of Si-ZSM-48 (CP contact times as indicated; the asterisks indicate an expanded intensity scale (×5)).

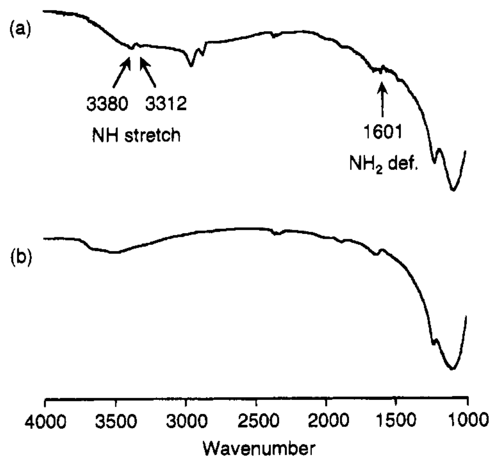

Figure 8. IR spectra of Si-ZSM-5 synthesized in the presence of hexanediamine and H_2O (a) and after calcination (b).

synthesis of Si-ZSM-48 reveal a different trend. As is expected, no polarization transfer is observed in the unheated gel. However, unlike the NMR results for the TPA- and hexanediamine-mediated syntheses of Si-ZSM-5, the appearance of efficient CP between the hexanediamine protons and the silicate species is not observed until long-range order is also detected by XRD and IR; the onset of CP does not precede the emergence of crystallinity. The intensities of the CP peaks then increase as the amount of crystalline material in the sample increases.

IR spectroscopic characterization of the HXN/Si-ZSM-5 and HXN/Si-ZSM-48 samples synthesized from a H_2O-containing gel suggests that hexanediamine is occluded as the neutral diamine rather than in the mono- or diprotonated form. In the spectrum of HXN/Si-ZSM-5 (Figure 8), the vibrational bands at 3380 and 3312 cm^{-1} correspond to NH stretches of a free amine, and the band at 1601 cm^{-1} is the NH_2 deformation mode;[23] the NH_3^+ stretching (2725 cm^{-1}) and NH_3^+ deformation modes (1564, 1505 cm^{-1}) expected for protonated hexanediamine are not observed.[23] It is reasonable that hexanediamine is also occluded as the neutral diamine in Si-ZSM-48,[24] although due to the low organic content the vibrations are too weak to be definitively assigned. The ^{13}C CP MAS NMR spectra of these products (not shown) are inconclusive regarding the protonation state of the organic species due to the broad linewidths of the resonances, but they are not inconsistent with the presence of the neutral diamine. When Si-ZSM-5 and Si-ZSM-48 are synthesized from a D_2O-containing gel, the characteristic IR vibrational modes of the diamine or its protonated forms are not observed. One possible explanation is that protonation and deprotonation of the amine groups during the synthesis ($pK_{a(1)} = 9.8$; $pK_{a(2)} = 10.9$;[25] synthesis gel pH > 12) results in H/D exchange, and that the mixture of NH_2, NHD, and ND_2 groups present in the occluded species results in multiple vibrational modes that are too low in intensity to be observed. However, only neutral hexanediamine is observed by liquid-phase ^{13}C NMR of the synthesis mixture (neutral diamine 26.9, 32.7, 41.4 ppm; diprotonated form 25.5, 26.9, 40.0 ppm; synthesis gel 27.0, 32.8, 41.5 ppm), which suggests that mono- or diprotonated hexanediamine is a minor (but potentially important) component of the synthesis mixture that produces Si-ZSM-5 and Si-ZSM-48.

In view of the plausible H/D exchange, the $^{1}H-^{29}Si$ CP NMR experiments with the hexanediamine require further comment. If H/D exchange occurs to a significant level, then the observed cross-polarization could be from protons not associated with the methylene carbons. However, it is clear from the data shown in Figure 7 that this is not the case. That is because no CP is observed until HXN/Si-ZSM-48 is formed. If the H/D exchange provided a significant proton content, then CP would be observed from protons in the solids collected prior to the formation of HXN/Si-ZSM-48. Likewise, with HXN/ZSM-5 (Figure 6), CP is observed when the organic is incorporated into the solid and increases as the organic content becomes larger.

Hydrophobic Hydration. The ^{29}Si MAS and $^{1}H-^{29}Si$ CP MAS NMR spectra of the unheated and heated (10 d at 110 °C) gels prepared with TMA, TEA, TPA, TBA, TPenA, and TEOA are shown in Figure 9; the spectra of unheated fumed silica (Cab-O-Sil) is also shown in Figure 9. In each of the ^{29}Si MAS NMR spectra, two resonances are observed, corresponding to Q^3 (−100 ppm) and Q^4 (−110 ppm) species. Efficient CP from the organic protons to silica does not occur in the unheated gels (note the expanded intensity scale relative to that in Figures 6 and 7); the CP spectra resemble that of Cab-O-Sil silica, in which there is some intramolecular polarization transfer from surface hydroxyl groups. The additional resonances in the spectra of the unheated TMA- and TEA-containing gels are assigned to the cubic octamer ($Si_8O_{20}^{8-}$) at −99 ppm (for TMA and TEA) and the prismatic hexamer ($Si_6O_{15}^{6-}$) at −89 ppm (for TMA only);[22] these species form readily in aqueous solutions of TMAOH or TEAOH but are not abundant in the presence of other tetraalkylammonium

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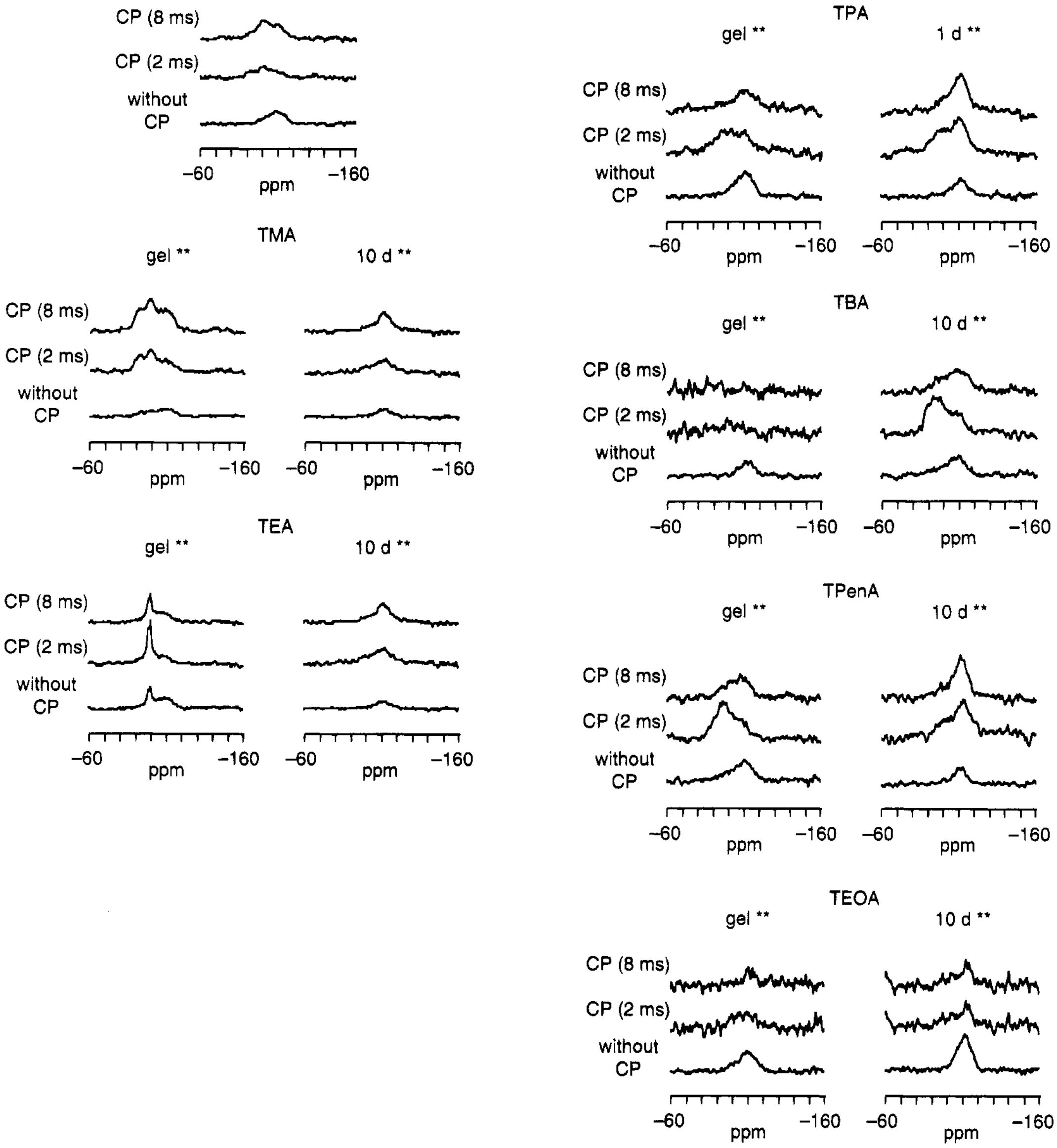

Figure 9. ^{29}Si MAS and ^{1}H−^{29}Si CP MAS NMR spectra of Cab-O-Sil and of the freeze-dried samples collected from synthesis gels containing TMA, TEA, TPA, TBA, TPenA, and TEOA (CP contact times as indicated; the asterisks indicate an expanded intensity scale (×25) relative to Figure 6, 60 day sample).

species.[26] ^{1}H−^{29}Si cross polarization to the double-ring silicate species is efficient due to the proximity of the charge-balancing TMA or TEA cations.[27]

After being heated for 10 days at 110 °C, all of the TAA-containing samples except for the TPA-containing synthesis mixture are amorphous by XRD and IR (not shown). Changes in the distributions of Q^3 and Q^4 species shown by the ^{29}Si MAS NMR spectra suggest that depolymerization and recondensation of the silica have occurred. Double-ring silicate species are no longer present in the TMA- or TEA-containing systems. Only a small amount of polarization transfer is observed in these spectra (except for those of TPA and perhaps TBA (vide infra)). For the TPA-containing sample, efficient CP is observed because some crystalline TPA/Si-ZSM-5 is present after 10 days of heating; the TPA-containing, X-ray amorphous sample after 1 day of heating provides a closer comparison to the other tetraalkylammonium-containing samples, although CP is still more efficient in the TPA-containing sample.

No crystalline products were formed from synthesis gels containing TEOA, even at higher synthesis temperatures. Using mixtures of TEOA and TPA, Si-ZSM-5 was formed in 4 days at 175 °C only when a sufficient amount of TPA was present in the gel to completely fill the void space of the zeolite product (TPA/Si = $^{1}/_{24}$; gel composition $0.21TPA_2O{:}0.29TEOA_2O{:}10SiO_2{:}380H_2O$). However, no TEOA was detected by ^{1}H−^{13}C CP MAS NMR in the product formed under these conditions (not shown). When a lower TPA content was used (TPA/Si = $^{1}/_{96}$; gel composition $0.05TPA_2O{:}0.45TEOA_2O{:}10SiO_2{:}380H_2O$), no crystalline material was obtained under the same conditions of heating time and temperature.

Crystallization Kinetics. The crystallization profiles of TPA/Si-ZSM-5, HXN/Si-ZSM-5, and HXN/Si-ZSM-48 are presented in Figure 10. In all cases, the presence of sodium appears to increase the rates of nucleation and crystal growth. Similarly, the use of

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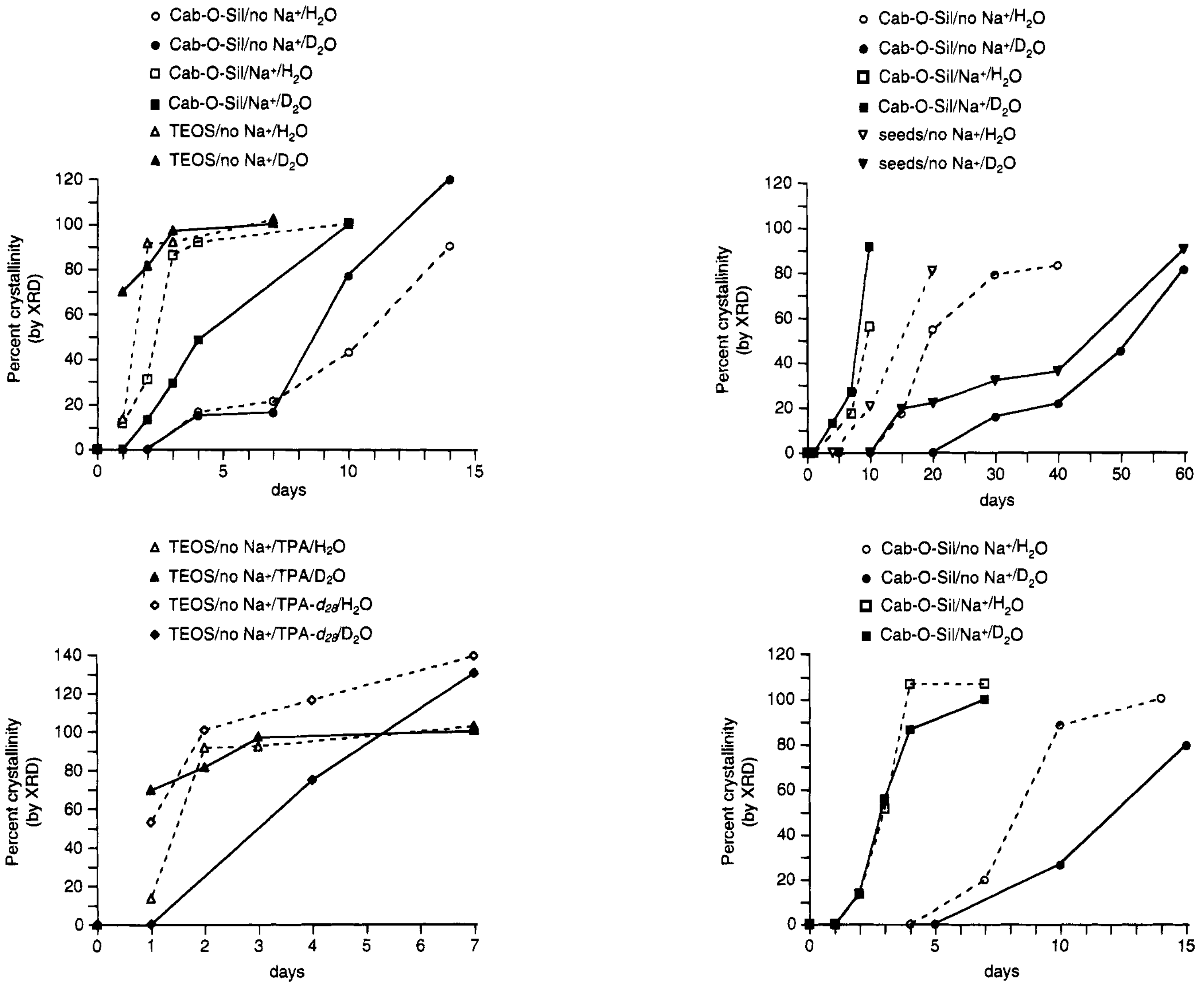

Figure 10. Crystallization profiles of TPA-mediated (a, top left), TPA-d_{28}-mediated (b, bottom left), and hexanediamine-mediated (c, top right) syntheses of Si-ZSM-5, and hexanediamine-mediated syntheses of Si-ZSM-48 (d, bottom right).

TEOS rather than fumed silica as the silica source enhances the rates of nucleation and crystallization for the synthesis of TPA/Si-ZSM-5. TEOS cannot be used for the hexanediamine-mediated synthesis of Si-ZSM-5 because the ethanol produced from the hydrolysis of TEOS apparently interferes with the gel chemistry or with an essential step in structure direction. Similarly, crystalline HXN/Si-ZSM-5 is not formed at 120 °C when 8 equiv of ethanol are added to a Cab-O-Sil-based synthesis gel. At 150 °C, however, HXN/Si-ZSM-48 is formed in 20 days using Cab-O-Sil and added ethanol; the slower rate of product formation is likely due to an effect of dilution by ethanol. Seeding of the synthesis of HXN/Si-ZSM-5 accelerates the rate of nucleation when fumed silica is used as the silica source.

In the absence of sodium or when a condensed silica source is used, a difference in the time of appearance of crystalline material in the growth curves is observed for syntheses performed in H_2O and D_2O solutions. The use of D_2O results in markedly delayed nucleation for the syntheses of TPA/Si-ZSM-5, HXN/Si-ZSM-5, and HXN/Si-ZSM-48. However, the rate of nucleation of Si-ZSM-5 is not affected when TPA-d_{28} was used in lieu of TPA.

Discussion

In the TPA-mediated synthesis of Si-ZSM-5, it has been proposed that a key step in the structure direction is the replacement of water molecules in the hydration sphere of TPA by silicate species to form inorganic–organic composite species.[1] Favorable overlap of the hydrophobic hydration sphere formed around TPA with the domains of hydrophobic hydration that are present at the siloxane bridges between two Q^4 groups in silica may be responsible for bringing the organic and inorganic components into proximity.[28] By contrast, Q^3 groups are hydrophilically hydrated and thus their hydration spheres may be incompatible with that of TPA despite the electrostatic attraction.[9,28,29] The release of water molecules from the ordered hydrophobic hydration spheres into the bulk and the subsequent establishment of favorable van der Waals contacts between the alkyl chains of TPA and the hydrophobic silica could thus provide the entropic and enthalpic driving forces for the formation of the composite inorganic–organic species; the entropic contribution arising from the

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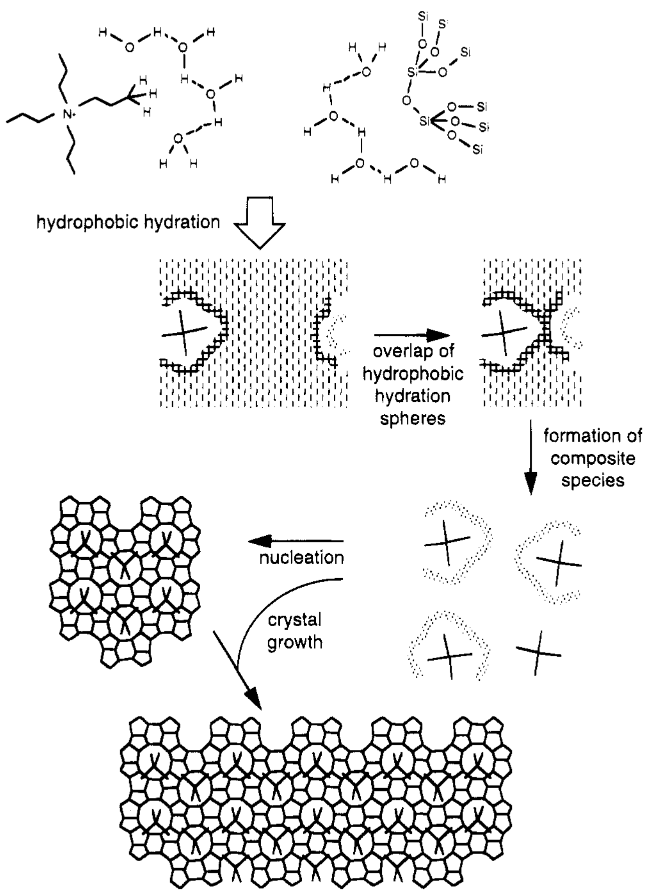

Figure 11. Proposed mechanism of structure direction in the TPA-mediated synthesis of Si-ZSM-5.

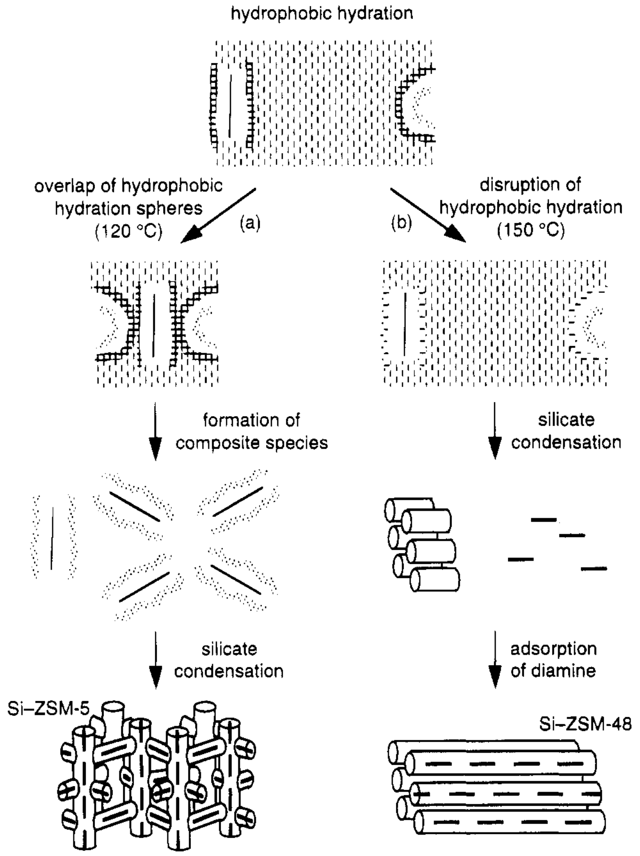

Figure 12. Proposed structure-directing (a) and space-filling (b) roles of hexanediamine in the syntheses of Si-ZSM-5 and Si-ZSM-48, respectively.

release of water from hydrophobic hydration spheres is analogous to that which has previously been described as an important component of the thermodynamic driving force for protein folding.[30] Efficient $^1H-^{29}Si$ CP in the X-ray amorphous, heated synthesis mixture provides evidence for the existence of close inorganic–organic contacts (without intervening water (D_2O) molecules) at an early stage during synthesis, which is consistent with the presence of these composite species in the synthesis of TPA/Si-ZSM-5. The intensities of the signals in the CP spectra increase as crystalline material is formed because the rigidity of the zeolite framework and the occluded organic molecules leads to stronger intermolecular H···Si dipolar interactions and thus to more efficient polarization transfer.[1,31] A proposed mechanism for the TPA-mediated synthesis of Si-ZSM-5 that incorporates all of these considerations is given in Figure 11.

In the hexanediamine-mediated synthesis of Si-ZSM-5, a similar correlation between the XRD and CP profiles is observed. Although no crystalline material is detected until after 30–40 days of heating, polarization transfer between the organic protons and the silicate species occurs in the X-ray amorphous, heated samples. Again, the observation of efficient intermolecular CP at an early stage in zeolite synthesis suggests that the organic and inorganic components are in close contact. Although the hydration behavior of hexanediamine has not been described in the literature, it is possible that hydrophobic hydration occurs in the vicinity of the alkyl backbone of the diamine molecule, with subsequent replacement of the water molecules by silicate species to form inorganic–organic composites. A small number of amine groups may be protonated and hydrophilically hydrated and thus may interact favorably with the soluble, anionic silicate species. However, hexanediamine is occluded in the final product as the neutral diamine and D^+ (H^+) apparently balance the charge of the anionic Q^3 sites present. Alternatively, the amine groups could form hydrogen bonds to water or interact with the amine groups of other diamine molecules, thus bringing the diamine molecules or composite species into close proximity and promoting the formation of the channel intersections of the Si-ZSM-5 structure. The presence of ethanol when TEOS is used as the silica source can influence these interactions and thus account for the observation that HXN/Si-ZSM-5 does not form when TEOS is used. A proposed mechanism for structure direction in the hexanediamine-mediated synthesis of Si-ZSM-5 similar to that proposed for the TPA-mediated synthesis is presented in Figure 12. Note that this mechanism is very speculative and is presented to stimulate discussion.

A structure-directing effect is not apparent in the hexanediamine-mediated synthesis of Si-ZSM-48. The difference in the interactions between the inorganic and organic components relative to those observed in the syntheses of Si-ZSM-5 could be due to the higher temperature at which Si-ZSM-48 is synthesized. At 150 °C, the hydration behavior of hexanediamine is different from that at 120 °C. Also, the silicate condensation

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chemistry at these conditions of concentration, pH, and temperature (150 °C) favor the formation of Si-ZSM-48 as long as an organic species is present. The observations that Si-ZSM-48 can be synthesized when ethanol is added and that the synthesis of Si-ZSM-48 is accessible through the use of several different organic bases[14] provide support for this explanation. By contrast, Si-ZSM-5 has only been synthesized in the presence of TPA or hexanediamine, although aluminosilicate ZSM-5 can be synthesized using other organic species or in an organic-free system;[14] for the aluminum-containing syntheses, structure formation is controlled by the aluminosilicate gel chemistry alone rather than by the inorganic–organic interactions that are apparently necessary for stabilization of pure-silica, crystalline microporous materials.[32,33] In the synthesis of Si-ZSM-48, the diamine molecules could adsorb into the void space of the zeolite as it crystallizes (pore filler) and stabilize the metastable inorganic material against dissolution in the basic synthesis medium. The occurrence of a specific structure-directing effect is not apparent, and hexanediamine serves simply as a pore-filling agent in the synthesis of Si-ZSM-48.

The effect of temperature in changing the role of an organic species (HXN) from that of a structure-directing agent (Si-ZSM-5 synthesis) to that of a pore-filling species (Si-ZSM-48 synthesis) is not universally applicable. Structure-directing effects from other organic species have been observed at synthesis temperatures above 150 °C.[14] If hydrophobic hydration is implicated in structure direction, then the temperature dependence of this effect will vary with the hydrophobicity of the specific species used; in general, the degree of hydrophobic hydration is decreased at higher temperatures and by some estimates may be absent at temperatures above 130–160 °C.[7] However, the use of lower synthesis temperatures is not necessarily the key factor in achieving structure direction because silicate dissolution and recondensation are less favorable at lower temperatures.[34]

The significance of hydrophobic hydration is investigated further in the series of synthesis mixtures containing different TAA cations and TEOA. In general, the degree of hydrophobic hydration is greater for species with longer alkyl chains.[6] TMA and TEA can be considered essentially as large, spherical or elliptical cations[35] with the charge located on the α-carbons.[36] TMA and TEA exhibit a somewhat different influence on the water structure than species with longer alkyl chains. Their hydration enthalpies are influenced primarily by electrostatic interactions, whereas those of TAA species with longer alkyl chains have both electrostatic and nonelectrostatic (hydrophobic hydration) contributions.[35] TPA and TBA behave as soluble, hydrophobic species and thus form hydrophobic hydration spheres. However, at high concentrations such as the concentration range used in zeolite synthesis ($\approx$0.3 M), TBA most likely exhibits a reduced hydrophobic hydration effect due to the formation of aggregates.[6] TPenA is not very soluble[11] and tends to aggregate and phase separate in aqueous solution rather than existing as isolated, hydrophobically hydrated cations. In contrast, the alcohol moiety of TEOA can participate in the hydrogen bonding network of water and thus does not form a hydrophobic hydration sphere despite the similarity in size to TPA.[6]

Among the TAA species investigated, a crystalline product is formed at the aforementioned synthesis composition and temperature only in the presence of TPA. In this case, intermolecular ^{1}H–^{29}Si polarization transfer is observed in the heated synthesis mixture prior to the formation of a crystalline product, which suggests that molecular organization events relevant to structure direction are occurring. Polarization transfer is not observed to a significant extent in samples prepared using TEOA or TAA species other than TPA, except when anionic double-ring silicate structures are present in the unheated, TMA- or TEA-containing gels. TMA and TEA must not be sufficiently hydrophobic to elicit interactions with hydrophobically hydrated silica, as is suggested by the observation that short-chain TAA ions do not adsorb onto silica as readily as long-chain species.[28] Also, if TMA or TEA interact with silica, they may be too mobile for intermolecular CP to occur.[1] On the other hand, TBA and TPenA most likely form aggregates, thus minimizing the extent of hydrophobic hydration and the potential for interaction with silica; nevertheless, a small amount of CP is observed for samples prepared using TBA. The ability of TBA to serve as a structure-directing agent for the synthesis of Si-ZSM-5 and Si-ZSM-11 at higher synthesis temperatures[32,37] may be due to the increased solubility of TBA (reduced tendency to aggregate). At temperatures above 110 °C, isolated TBA molecules must exhibit the appropriate hydrophobic hydration for inorganic–organic composite species to subsequently form; the possibility that the necessary interactions between silicate and TBA could be established at higher temperatures is suggested by the observation of some CP in the TBA-containing samples prepared at 110 °C. By contrast, TEOA interacts preferentially with water via hydrogen bonding of the alcohol moiety rather than interacting with silica. Thus, the observation of intermolecular CP in the X-ray amorphous, heated synthesis mixture appears to correlate with the observation of a structure-direction effect; only when Si-ZSM-5 is eventually formed is efficient CP observed in the heated, X-ray amorphous precursor.

An explanation of the molecular level interactions that are relevant to the presence or absence of a structure-directing effect and are reflected by the ^{1}H–^{29}Si CP profiles needs to be clarified in order to move toward the ultimate goal of the a priori design of effective structure-directing agents. In particular, it is of interest whether the ability to form a hydrophobic hydration sphere is a requisite property for a species to serve as a structure-directing agent. Alternatively, the molecular characteristics that induce hydrophobic hydration may also be those that generate the requisite favorable organic–inorganic interactions in the zeolite product, without hydrophobic hydration spheres playing

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a role in the mechanism of structure direction. It has been shown that although the thermodynamic driving force for the synthesis of TPA^+F^-/Si-ZSM-5 from amorphous silica is dominated by the enthalpically favorable, inorganic–organic van der Waals interactions within the product ($\Delta H \approx -1.5$ kcal (mol of $SiO_2)^{-1}$), there is an entropic contribution resulting from the release of ordered water molecules from the hydrophobic hydration sphere of TPA in going from the synthesis solution into the zeolite ($-T\Delta S \approx -0.4$ kcal (mol of $SiO_2)^{-1}$).[33] TPA/Si-ZSM-5 likely represents a nearly optimum case for inorganic–organic van der Waals interactions in zeolite synthesis; when the intermolecular interactions are less favorable and the enthalpic contribution to the driving force is thus less strong, it is possible that the entropic factor arising from the release of water from the hydrophobic hydration sphere of the organic species may be a predominant factor in determining whether the formation of inorganic–organic composite species and a crystalline product are thermodynamically favored. The observation that no crystalline product is obtained using TEOA even when a small amount of TPA (sufficient for nucleation to occur) is present suggests that the formation of a hydrophobic hydration sphere is significant to the mechanism of structure direction. However, these results do not provide a clear distinction between the role of enthalpic and entropic considerations, and further investigation is warranted.

All molecules that form hydrophobic hydration spheres may not necessarily exhibit structure-directing effects. It has been suggested that the ability of an organic molecule to serve as a structure-directing agent lies in a delicate balance of hydrophilic properties that provide solubility in aqueous solution and hydrophobic character, which generates favorable interactions with the crystalline silica host.[32,38,39] Although TPA is the only member of the series of homoleptic TAA species that has the proper balance of hydrophobic and hydrophilic properties to serve as a structure-directing agent at the synthesis composition and temperature investigated (TBA can be used to synthesize Si-ZSM-5 and Si-ZSM-11 at higher temperatures (vide supra)), nonsymmetric quaternary alkylammonium species may be found that exhibit these characteristics. Zones has demonstrated a correlation between the C/N^+ ratios (an estimate of hydrophobic or hydrophilic character) of various quaternary alkylammonium species and the extent to which these species transfer from aqueous solution to a chloroform phase;[39] for molecules with C/N^+ ratios less than 11, a small degree of transfer (<10%) occurs, whereas for molecules with C/N^+ ratios greater than 15, a large degree of transfer (>70%) occurs. The observation that many of the species investigated that have intermediate C/N^+ ratios ($11 < C/N^+ < 15$) serve as structure-directing agents in the synthesis of high-silica zeolites supports the suggestion that a balance of hydrophilic and hydrophobic properties is important for structure-directing ability.[39]

All of the mechanistic considerations up to this point have been thermodynamic ones. However, zeolites are metastable relative to quartz, and thus zeolite synthesis is a kinetically controlled process.[16,40] The crystallization profiles demonstrate that several factors in the synthesis mixture can influence the rates of nucleation and crystal growth of Si-ZSM-5 and Si-ZSM-48, even in the presence of a structure-directing agent. The more rapid nucleation that occurs when sodium is present or when a monomeric silica source (TEOS) is used suggests that nucleation in the TPA-mediated synthesis of Si-ZSM-5 and in the hexanediamine-mediated syntheses of Si-ZSM-5 and Si-ZSM-48 is limited by the rate of dissolution of the highly-condensed silica source (Cab-O-Sil) that is used. Sodium has been shown to enhance the rate of dissolution of quartz,[41,42] and it is thus consistent that nucleation is dependent on the rate at which soluble silicate species are made available to form inorganic–organic composites. The rate of crystal growth appears also to be limited by the availability of soluble silicate and is thus enhanced by the presence of sodium in low concentrations. At high concentrations of sodium, the structure-directing influence of sodium is predominant over that of the organic species, and layered silicates with a large proportion of anionic Q^3 sites are formed for optimum electrostatic interactions.[33,43] The observation that nucleation of HXN/Si-ZSM-5 from a seeded synthesis mixture is faster than that from the nonseeded preparation but slower than that from a sodium-containing gel suggests that the rate of nucleation is not determined solely by the rate of dissolution of silica; otherwise, similar rates would be expected for the sodium-containing and seeded syntheses. Sodium must also facilitate the association, orientation, and condensation of the inorganic–organic composite species within aggregates of the appropriate size (≈50–60 Å) to form nuclei.[44,45]

In the absence of the accelerating influences of sodium or TEOS, the slowed rates of nucleation for syntheses using D_2O in lieu of H_2O are noteworthy. The existence of an isotope effect suggests that cleavage of O–H or O–D bonds figure in rate-determining steps in the nucleation process. However, it is not likely that this effect simply involves the base-catalyzed dissolution of silica since OD^- is a stronger base than OH^-; the presence of OD^- would be expected to accelerate rather than decelerate the dissolution process.[15] The hydrogen bonding network of D_2O is more strongly bonded than that of H_2O,[6] and thus restructuring of the network to allow the organic and silicate components to come into contact in order for nucleation to occur may be slowed in D_2O. There could also be a decelerating influence of D_2O on the silicate condensation chemistry due to the slower rates of O–D bond formation and cleavage,[15] which may lead to slower nucleation and crystal growth. However, the similar rates of nucleation in the syntheses comparing TPA and TPA-d_{28} in H_2O demonstrate that direct hydrogen bonds between the organic and inorganic (H_2O or silica) components must not be

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present; if such bonds were involved, observation of an isotope effect would be expected in the presence of TPA-d_{28}. Thus, the observed kinetics of nucleation are consistent with a mechanism that includes the formation of inorganic–organic composite species via favorable van der Waals interactions as a key step.

Proposed Mechanism. The fundamental aspects of the previously proposed mechanism of structure direction and self-assembly in the TPA-mediated synthesis of Si-ZSM-5 are supported by the present results (Figure 11). The key step in this process is the formation of inorganic–organic composite units that then provide the primary species involved in zeolite nucleation and crystal growth. The ability of TPA to form a hydrophobic hydration sphere is an important factor in structure direction because favorable overlap of the hydrophobic hydration sphere formed around the organic species with the hydrophobically hydrated domains of the soluble silicate species may be responsible for bringing the organic and inorganic components into proximity.[28] Favorable van der Waals contacts between the alkyl chains of TPA and hydrophobic silica are established upon release of water molecules from the ordered hydration spheres into the bulk;[32] this process could be slowed in the presence of D_2O due the more structured hydration sphere that must be reorganized. The establishment of van der Waals interactions and the release of ordered water molecules provide the thermodynamic driving force for the formation of inorganic–organic composite species.[33] Optimization of van der Waals interactions within these species gives rise to the geometric correspondence between the organic molecules and the inorganic architecture that is characteristic of the structure direction phenomenon.

The availability of soluble silicate influences the rate at which these composite species are formed; the use of a monomeric silica source such as TEOS or the presence of sodium in the synthesis mixture to facilitate dissolution of a condensed silica precursor results in an enhanced rate of nucleation. When a critical concentration of the inorganic–organic composite species is present, aggregation of these species likely leads to nucleation;[44,46] this process can occur in solution or on the surface of silica particles[44] or the walls of the reaction vessel (heterogeneous nucleation). Subsequent crystal growth can occur via the attachment of composite species to the crystallite surface in a layer-by-layer fashion,[1] as suggested by the layered structure of ZSM-5/ZSM-11 intergrowths[47] and other intergrowths of high-silica zeolites.[48-50] Free TPA molecules (and additional organic molecules that may have been introduced into the synthesis mixture, such as TMA or TEA)[51] and silicate species may also be able to diffuse to the surface of the growing zeolite crystal and be incorporated into the crystalline structure.

It is possible that the mechanism can be generalized to other examples of structure direction in the synthesis of known and novel high-silica and pure-silica zeolites. If the organic species exhibits the appropriate balance of hydrophobic and hydrophilic character, a sufficient extent of hydrophobic hydration can occur in solution such that the formation of inorganic–organic composite species is favored. It may be possible to screen potential organic structure-directing agents by observing their interactions with silicate species via the $^{1}H-^{29}Si$ CP MAS NMR technique. Although the precise details of the organic–silicate interactions (or lack of interactions) are not elucidated in our studies, it is clear that syntheses that exhibit $^{1}H-^{29}Si$ CP NMR signatures also show structure direction (two examples), and those that do not either result in pore-filling of organics (HXN/Si-ZSM-48) or the lack of crystal formation (five examples).

Acknowledgment. Financial support of this work has been provided by the Chevron Research and Technology Co. The authors thank Dr. Stacey Zones of the Chevron Research and Technology Co. for numerous helpful discussions. The authors also thank Professor R. A. van Santen and Dr. T. P. M. Beelen for preprints of their work.

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