

Mechanisms of Structure Direction in the Synthesis of Pure-Silica Zeolites. 1. Synthesis of TPA/Si-ZSM-5

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The role of tetrapropylammonium (TPA) as a structure-directing agent in the sodium-free synthesis of pure-silica ZSM-5 (Si-ZSM-5) is investigated by solid-state ^1H - ^{29}Si CP MAS NMR. It has previously been proposed that the mechanism of structure direction in a sodium-containing system involves preorganization of silicate species around the TPA ions with subsequent assembly of these inorganic-organic composite structures to yield crystalline Si-ZSM-5 with occluded TPA molecules.¹ ^1H - ^{29}Si CP MAS NMR results indicate that short-range intermolecular interactions, *i.e.*, on the order of van der Waals contact distances, are established during heating of the zeolite synthesis gel prior to the development of long-range order indicative of the ZSM-5 structure. These interactions are independent of the presence of sodium in the gel or the silica source used. An attempt to isolate the composite species by trimethylsilylation of the synthesis mixture was partially successful. These results provide additional evidence for the existence of preorganized, inorganic-organic composite structures during the synthesis of Si-ZSM-5. A modified mechanism of structure direction and crystal growth of Si-ZSM-5 is proposed.

Introduction

The routes by which crystalline zeolites are produced from an amorphous aluminosilicate or silicate gel are complex self-assembly processes that involve numerous simultaneous and interdependent equilibria and condensation steps. Consequently, zeolite crystallization is not well understood, except in that there does not appear to be a universal mechanism to describe all zeolite syntheses.² The addition of organic molecules such as amines and alkylammonium ions to zeolite synthesis gels can affect the rate at which a particular material is formed or can make new structures or framework chemical compositions accessible. However, the exact role of the organic species and the mechanism by which they affect the formation of the product structure remain to be elucidated.^{2,3} In particular, the nature and extent of interactions between the organic and inorganic components of a zeolite synthesis gel are not well defined. These interactions may be the key to understanding why in some zeolite syntheses there is a strong correlation between the geometry of the organic molecule and the zeolite pore architecture (the organic species serves as a structure-directing agent) while in other syntheses no such relationship is observed (the organic species serves as a space-filling agent).

ZSM-5 (MFI topology) is one of the most widely studied and commercially important zeolites. The MFI structure consists of parallel, linear, 10-ring channels intersected by 10-ring sinusoidal channels. When pure-silica ZSM-5 (Si-ZSM-5) is synthesized using the tetrapropylammonium (TPA) cation as the organic struc-

ture-directing agent, the TPA molecules are located at the channel intersections with the propyl chains extending into both the linear and sinusoidal channels.^{4,5} The molecules are held tightly at these sites and can be removed only by calcination; they cannot diffuse in to or out of the structure. Tight enclathration of the TPA molecules suggests that they must be incorporated into the silicate structure during the process of crystal growth. In a previous study, a mechanism of structure direction (the term structure direction is normally used to imply a tight fit of the organic molecule in the inorganic host, *e.g.*, pure-silica ZSM-5, ZSM-18, and SSZ-33, while loosely held organics more likely function as pore-filling agents, *e.g.*, mordenite, $\text{AlPO}_4\text{-5}$ ²) in the TPA-mediated synthesis of Si-ZSM-5 was proposed based on the results of ^1H - ^{29}Si CP MAS NMR.¹ The reported NMR data suggest that upon heating of the D_2O -containing synthesis gel, close contact between the protons of TPA and the silicon atoms of the inorganic phase is established prior to the formation of the long-range order of the crystalline zeolite structure; the work of Mentzen and co-workers suggests that the $\text{H}\cdots\text{Si}$ interatomic distance necessary for efficient ^1H - ^{29}Si CP is approximately that of a van der Waals interaction (≈ 3.3 Å).⁶ No analogous intermolecular ^1H - ^{29}Si CP occurs when a non-structure-directing organic species, *e.g.*, tetramethylammonium (TMA), is used in lieu of TPA, suggesting that intermolecular interactions observed by the CP technique are relevant to structure direction. For the TPA-mediated synthesis of Si-ZSM-5, it was thus proposed that silicate is closely associated with the TPA molecule to form inorganic-organic

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composite species that are the key species in the nucleation and crystal growth processes for the self-assembly of Si-ZSM-5.

The present work provides additional insight into the nature and occurrence of these composite species. Using the technique of intermolecular ^1H - ^{29}Si CP MAS NMR, the influence of the inorganic components of the synthesis mixture, *e.g.*, the presence of sodium or the use of different silica sources, on the mechanism of structure direction and the kinetics of product formation is investigated for the TPA-mediated synthesis of Si-ZSM-5.⁷ An attempt to isolate the relevant preorganized, intermediate species by capping the Si-OH groups of the various silicate species in solution with trimethylsilane with subsequent separation of the species of interest is described.⁷

Experimental Section

Synthesis. A sodium-free synthesis procedure for Si-ZSM-5 was developed in which the only sources of protons are the organic structure-directing agent and its hydroxide counterion. The gel composition for the synthesis of Si-ZSM-5 was $0.5\text{TPA}_2\text{O}:10\text{SiO}_2:380\text{D}_2\text{O}$. An approximately 0.5 M solution of TPAOH in D_2O was prepared using Amberlite IRA-400 (OH) anion-exchange resin (Aldrich) and TPABr (Aldrich) in D_2O (Cambridge Isotope Laboratories, 99.9 atom % D); the exact concentration of TPAOH was determined by titration with 0.096 N HCl (Aldrich). In a typical synthesis of Si-ZSM-5, a gel containing 5.23 g of TPAOH solution, 14.22 g of D_2O , and 1.5 g of fumed SiO_2 (Cab-O-Sil, Grade M-5) was stirred for 3 h. The fluid gel was heated at 110 °C in Teflon-lined stainless steel reactors for 15 days. Samples were collected from the unheated gel and after 1, 10, and 15 days of heating; sample collection was difficult since some nucleation occurred on the surface of the Teflon liner, rendering the crystalline solid difficult to isolate. The samples were freeze-dried by immediate quenching of the hot gels in liquid N_2 , with subsequent removal of D_2O by sublimation at -4 °C in vacuo.¹ When tetraethylorthosilicate (TEOS, Aldrich) was instead used as the silica source, the synthesis mixture was a clear solution. Samples were collected from the unheated solution and after 1, 4, and 7 days of heating; crystallization was complete in 7 days.

A sample of Si-ZSM-5 was also prepared using deuterated TPA (TPA- d_{28}) and TEOS using a gel composition of $0.5(\text{TPA-}d_{28})_2\text{O}:10\text{SiO}_2:380\text{H}_2\text{O}$. (TPA- 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. Zeolite crystallization was complete after 7 days of heating at 110 °C.

Silylation of silicate species in the unheated, TEOS-containing synthesis mixture was performed according to the procedure of Agaskar.⁸ An aged synthesis mixture prepared from 0.84 g of 40 wt % TPAOH in H_2O (Johnson Matthey), 10.9 g of H_2O , and 3.5 g of TEOS was added dropwise to a solution containing 2.34 g of hexamethyldisiloxane (Aldrich), 18.1 g of 2,2-dimethoxypropane (Aldrich), and 1.10 g of concentrated HCl (Fisher) and stirred for 1 h at room temperature. After concentration in vacuo at room temperature to remove the volatile components of the silylation reaction mixture, a solution containing 2.34 g of hexamethyldisiloxane, 5.8 g of *N,N*-dimethylformamide (DMF, Aldrich), and 1.31 g of trimethylchlorosilane (Aldrich) was added and stirred for 1 h to complete the silylation process. *n*-Pentane and water were added to the resulting solution and stirred for 5 min. The two-phase mixture contained a white solid suspended in the organic phase. The aqueous phase was extracted four times

with *n*-pentane. Filtration of the combined organic phases yielded a fine, white powder.

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 high-power proton and X-channel amplifiers. Samples were packed under a dry N_2 or Ar atmosphere into 7 mm ZrO_2 rotors and spun at 1-3 kHz. ^{29}Si spectra (59.63 MHz) were collected using MAS (8 s recycle time) or ^1H - ^{29}Si CP MAS with ^1H decoupling (4 s recycle time; 2-8 ms contact time) and were referenced to a tetrakis(trimethylsilyl)silane external standard (downfield resonance at -10.05 ppm vs tetramethylsilane (TMS)); ^{29}Si chemical shifts are reported relative to TMS. Exponential line broadening of 50 Hz was applied to the data. ^{13}C spectra of TPA-containing samples (75.47 MHz) were obtained using ^1H - ^{13}C CP MAS with ^1H decoupling (2 s recycle time, 2 ms contact time) or ^1H decoupling only (2 s recycle time) and were referenced to an adamantane external standard (downfield resonance at 38.4 ppm vs TMS); ^{13}C chemical shifts are reported relative to TMS. Exponential line broadening of 20 Hz (unwashed samples) or 100 Hz (washed samples) was applied to the data. Spectral fitting was performed using Bruker LINESIM software.

Solution-phase ^1H (300.10 MHz) and ^{13}C (75.47 MHz) NMR spectroscopy of the silylated material was performed using a General Electric QE 300 spectrometer. ^1H spectra were obtained using a 10 μs 90° pulse and a 4 s recycle time. ^{13}C spectra were obtained with ^1H decoupling using a 30° pulse of 3.47 μs and a recycle time of 1 s. Chemical shifts were referenced to tetramethylsilane. Solution phase ^{29}Si NMR (99.36 MHz) was performed using a Bruker AM 500 spectrometer. ^1H -decoupled spectra were obtained using a 90° pulse of 13.5 μs and a recycle time of 5 s. Chromium(III) acetylacetonate was added as a relaxation agent.

X-ray powder diffraction (XRD) data were collected on a Scintag XDS-2000 diffractometer using Cu K α 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 ($23.19^\circ 2\theta$; (501) reflection) to the height of the 501 reflection of the Si-ZSM-5 sample 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 intensity of the 501 reflection and the percent crystallinity are zero.

IR spectroscopy was performed on a Nicolet System 800 FTIR Instrument. IR samples were prepared as KBr pellets. Raman spectroscopy was performed using the Fourier Transform Raman Accessory (Nd:YAG laser; $\lambda = 1064$ nm; 600 mW) for the Nicolet System 800 FTIR.

Thermogravimetric analyses (TGA) were performed on a DuPont 951 thermogravimetric analyzer. Approximately 10 mg of sample were heated at a rate of 5 °C min^{-1} to 600 °C. Elemental analysis (C, H, N, Si, Na) was performed at Galbraith Laboratories, Knoxville, TN. Time-of-flight mass spectrometry was performed by Jane Sanders at the California Institute of Technology.

Results

Influence of the Silica Source. The crystallization profiles for the syntheses of Si-ZSM-5 in the presence of TPA are shown in Figure 1; they are also compared to the crystallization profile for the previously reported mechanistic investigation of the synthesis of Si-ZSM-5, in which sodium was present in the gel.¹ When a monomeric silica source (TEOS) is used, nucleation and crystal growth occur more rapidly than when a highly condensed source of silica such as Cab-O-Sil is used. For the synthesis using TEOS, crystallization begins in less than 1 day of heating and is complete after 7 days. By contrast, crystallization of Si-ZSM-5 from a condensed

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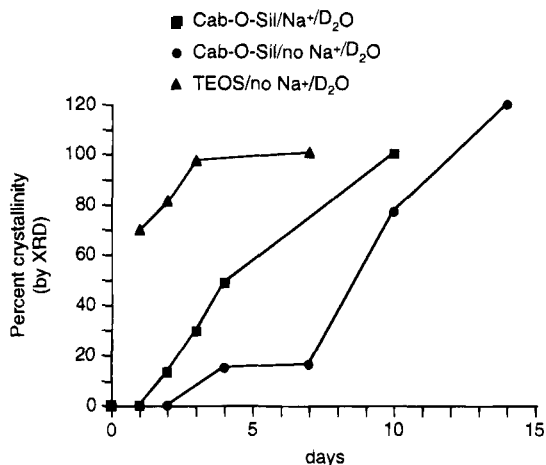


Figure 1. Crystallization profiles of TPA-mediated syntheses of Si-ZSM-5.

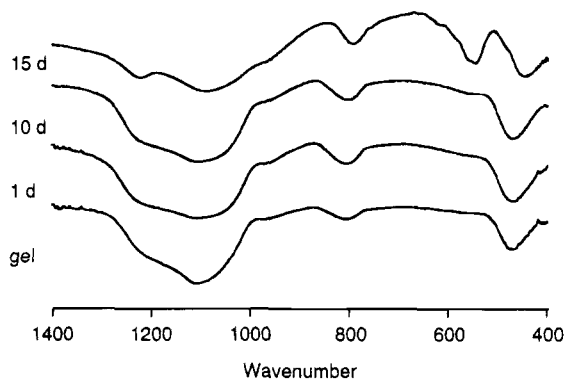


Figure 2. IR spectra of the D₂O-washed, freeze-dried samples collected during the TPA-mediated synthesis of Si-ZSM-5 using Cab-O-Sil.

silica precursor involves a 2–4 day induction period before crystalline product is detected by XRD.

The IR spectrum of Si-ZSM-5 is characterized by two structural vibrational bands in the spectra region of 400–700 cm⁻¹: one at 550–560 cm⁻¹,⁹ which has not been conclusively assigned but may be a stretching mode of structural silicate double-ring units,¹⁰ and one at 440–470 cm⁻¹, which is a Si–O bending mode observed in many polymorphs of SiO₂.¹¹ The appearance of the 550–560 cm⁻¹ band is indicative of the atomic ordering of Si-ZSM-5 and is not observed in amorphous silica, TEOS, or TEOS hydrolyzed in the presence of sodium hydroxide. The spectroscopic signature is apparent even in samples that are apparently amorphous by conventional X-ray techniques and most likely contain domains of Si-ZSM-5 that are on the order of only a few unit cells (length scale <80 Å).⁹ For the synthesis using condensed silica, the appearance of the 550–560 cm⁻¹ band in the spectrum of the washed, freeze-dried samples is concurrent with the development of peaks in the XRD pattern, *i.e.*, after 5–10 days of heating (Figure 2). However, in the IR spectra obtained during the synthesis of Si-ZSM-5 using TEOS, a band

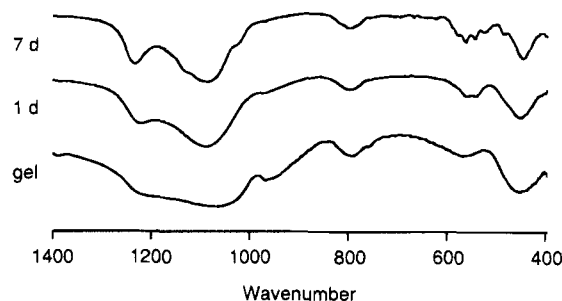


Figure 3. IR spectra of the D₂O-washed, freeze-dried samples collected during the TPA-mediated synthesis of Si-ZSM-5 using TEOS.

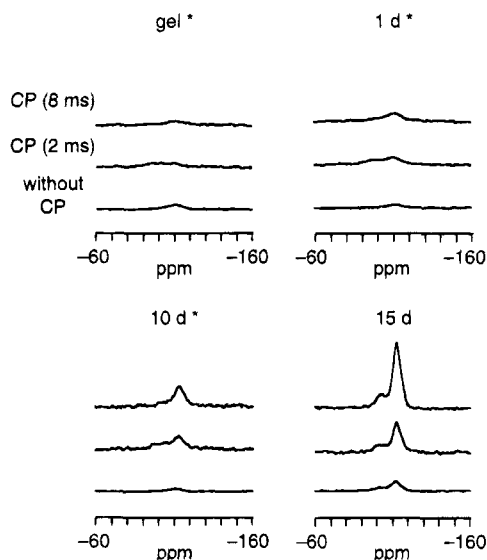


Figure 4. ²⁹Si MAS and ¹H–²⁹Si CP MAS NMR spectra of the freeze-dried samples collected during the TPA-mediated synthesis of Si-ZSM-5 using Cab-O-Sil (CP contact times as indicated; asterisks indicate an expanded intensity scale (×5)).

is apparent at 560 cm⁻¹ in the spectrum of the X-ray amorphous, freeze-dried, unheated synthesis mixture as well as in those of all of the partially or fully crystalline samples obtained after heating (Figure 3).

TGA of the crystalline products indicates two stages of weight loss: the first, from 25 to 345 °C corresponds to desorption of water, and the second, from 345 to 600 °C, corresponds primarily to combustion of TPA, with perhaps some additional desorption of water due to silanol condensation; calculation of the weight percent of TPA from the weight loss above 345 °C may thus overestimate the TPA content. On the basis of TGA data, the crystalline products have similar unit-cell compositions (4.6TPA:96SiO₂:1.5D₂O for the synthesis using Cab-O-Sil; 4.4TPA:96SiO₂:2.3D₂O for the synthesis using TEOS); ZSM-5 cannot contain more than 4 TPA molecules per 96 SiO₂ units.

The ²⁹Si MAS and ¹H–²⁹Si CP MAS NMR spectra of freeze-dried samples synthesized using Cab-O-Sil and TEOS are shown in Figures 4 and 5. An *in situ* ¹H–²⁹Si CP MAS NMR study was not possible for this system because of the large amount of water (D₂O) present; the species within the system are too mobile to permit efficient cross polarization. The freeze-dry technique was employed in order to preserve the silicate structures that are present at synthesis conditions and to avoid the appearance of structural artifacts that may result from slow cooling of the sample and filtration to

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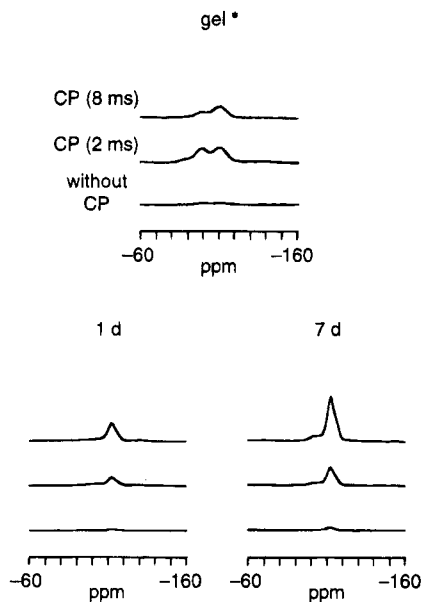


Figure 5. ^{29}Si MAS and ^1H - ^{29}Si CP MAS NMR spectra of the freeze-dried samples collected during the TPA-mediated synthesis of Si-ZSM-5 using TEOS (CP contact times as indicated; asterisks indicate an expanded intensity scale ($\times 5$)).

collect the solid phase.¹² Subsequent washing of the freeze-dried samples with D_2O did not significantly alter the cross polarization profiles. ^1H - ^{29}Si CP MAS NMR spectra are shown at two different contact times to demonstrate the degree of molecular motion within the samples. For relatively immobilized systems and short contact times (≤ 10 ms), a greater extent of polarization transfer is achieved with increasing contact time because polarization is transferred to more distant nuclei as well as to nuclei within the van der Waals contact distance; however, spin-lattice relaxation of the spin-locked protons becomes significant at long contact times (> 10 ms), thus reducing the extent of polarization transfer.¹³

The two resonances in the spectra in Figures 4 and 5 correspond to Q^3 (downfield resonance) and Q^4 (upfield resonance) species (Q^n represents $\text{Si}(\text{OSi})_n(\text{OD})_{4-n}$). 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.¹⁴ The appearance of a peak in the CP spectrum suggests that the protons of TPA and the silicon-containing species are in close proximity, *i.e.*, within the van der Waals contact distance ($\text{H} \cdots \text{Si}$ interatomic distance $\approx 3.3 \text{ \AA}$),⁶ without intervening water (D_2O) molecules;¹ CP is most efficient in the crystalline products. When a condensed source of silica is used (Figure 4), no CP is observed in the unheated gel because the TPA molecules cannot interact with the bulk silica; they can only interact with the

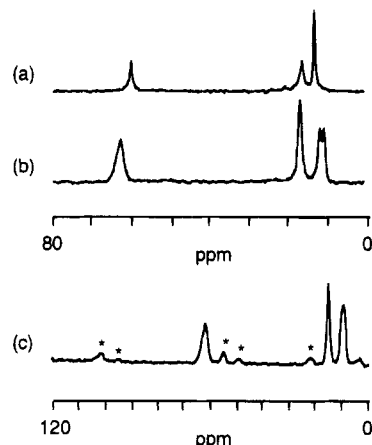


Figure 6. ^1H - ^{13}C CP MAS NMR spectra of TPABr (a); TPA occluded in Si-ZSM-5 (b); and TPA- d_{28} occluded in Si-ZSM-5 (c) (asterisks indicate spinning sidebands).

surface of the undissolved silica particles. After heating of the synthesis mixture, intermolecular polarization transfer is observed, even prior to the appearance of long-range order of Si-ZSM-5 by XRD or IR. Even at the shorter contact time measured (2 ms), the intensity of the CP spectrum is greater than that obtained without CP, suggesting that polarization transfer is efficient; for nondeuterated zeolite systems, the intensity of the spectrum obtained with CP is generally weaker than that obtained without CP¹⁵ since the presence of mobile H_2O provides an additional pathway for proton relaxation. At the shorter contact time, Q^3 species are polarized more rapidly than Q^4 species, perhaps because the Q^3 species are in closer proximity to the organic protons due to a weak coulombic attraction; nonprotonated Q^3 sites ($\text{Si}(\text{OSi})_3(\text{O}^-)$) apparently provide the charge-balancing anions for TPA cations occluded in crystalline Si-ZSM-5.¹⁶ At a longer contact time, more distant Q^4 sites are more strongly enhanced. For the partially and completely crystalline samples obtained at heating times of 5–15 days, the CP profiles follow the same trend with a substantial overall increase in signal intensity of all of the CP spectra. The spectra obtained without CP provide no additional mechanistic information. However, these spectra indicate that 20–25% of the Si atoms in the as-synthesized, crystalline Si-ZSM-5 samples are Q^3 sites, although a content of only 4% nonprotonated Q^3 is required for charge balance of the TPA cations. An understanding of the origin and nature of the additional Q^3 sites in these samples is currently under investigation.

When a monomeric silica source is used, polarization transfer is observed not only in the heated, partially or fully crystalline samples but also in the unheated synthesis mixture (Figure 5). The observed CP is not due to the presence of protons from nonhydrolyzed TEOS or from ethanol produced by hydrolysis since these species are removed by freeze-drying (*vide infra*).

The ^1H - ^{13}C CP MAS NMR spectra of solid TPABr, TPA occluded into Si-ZSM-5, and TPA- d_{28} occluded in Si-ZSM-5 are shown in Figure 6. When the TPA cation

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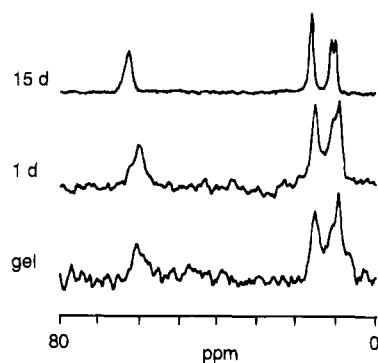


Figure 7. ^1H - ^{13}C CP MAS NMR spectra of the D_2O -washed samples collected from the synthesis of Si-ZSM-5 using Cab-O-Sil.

is located in the channel intersections of Si-ZSM-5, its spectrum is markedly changed from that of TPABr.^{17,18} The former is characterized by a downfield shift and broadening of the resonance of the methylene carbon adjacent to the nitrogen group (60.0 ppm for TPABr; 62.6 ppm for occluded TPA) and an upfield shift and splitting of the methyl carbon resonance (12.6 ppm for TPABr; 10.1 and 11.3 ppm for occluded TPA), while the resonance of the second methylene carbon remains essentially unchanged (16.0 ppm for TPABr; 16.3 ppm for occluded TPA). The spectral signature of occluded TPA reflects the change in conformation and the changes in intramolecular and intermolecular van der Waals interactions that are imposed on TPA upon occlusion into the channel intersections of Si-ZSM-5.¹⁷⁻¹⁹ TPA in TPABr has an S_4 axis at the nitrogen center and an all-trans conformation in the alkyl chains,²⁰ while occluded TPA has approximate C_s symmetry at the nitrogen center and some gauche interactions in the alkyl chains.⁵ Although the splitting of the methyl carbon resonance of TPA occluded in ZSM-5 has previously been attributed to steric contact between the methyl groups of two adjacent TPA molecules,¹⁸ the absence of splitting of the methyl resonance in the ^{13}C MAS NMR spectrum of sterically bulkier TPA- d_{28} occluded in Si-ZSM-5 (9.4 ppm; 15.3 ppm; 61.8 ppm) suggests that the splitting does not arise from methyl-methyl interactions. The splitting of the methyl carbon resonance is likely due to differences in the van der Waals interactions between the methyl groups and the silicate framework in the straight and sinusoidal channels. van der Waals interactions between TPA and the silicate structure are also responsible for the upfield shift of the methyl carbon resonance relative to that of TPABr.

For the ^1H - ^{13}C CP MAS NMR spectra of the washed, freeze-dried samples collected during the synthesis Si-ZSM-5 using Cab-O-Sil as the silica source, some TPA is evident in the X-ray amorphous material (9.5, 15.5, 60.4 ppm, Figure 7). However, the channel intersections of Si-ZSM-5 are apparently not fully formed, as suggested by the resonance of the methylene carbon adjacent to nitrogen. Upon further heating and the appearance of crystalline Si-ZSM-5 in the XRD pattern,

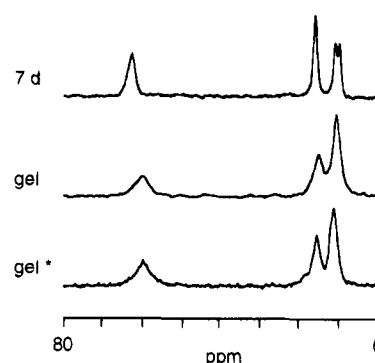


Figure 8. ^1H - ^{13}C CP MAS NMR spectra of the D_2O -washed samples collected from the synthesis of Si-ZSM-5 using TEOS (the asterisk indicates unwashed sample).

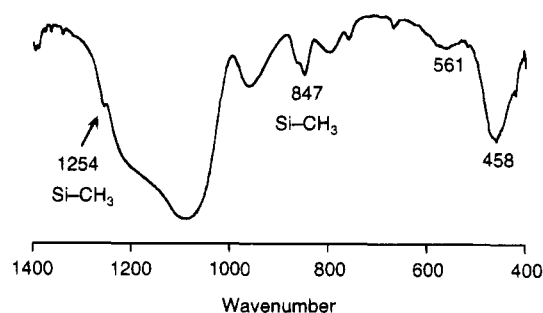


Figure 9. IR spectrum of the sample collected by trimethylsilylation of the unheated, TEOS-containing synthesis mixture.

the characteristic ^1H - ^{13}C CP MAS NMR spectrum of TPA occluded in Si-ZSM-5 is observed.

For the ^1H - ^{13}C CP MAS NMR spectrum of the unheated, TEOS-containing synthesis mixture, a substantial amount of TPA is present in the washed, freeze-dried sample (Figure 8); residual, nonhydrolyzed TEOS and ethanol produced by the hydrolysis of TEOS are not observed in the ^1H - ^{13}C CP MAS NMR spectrum of the unwashed sample because they have been removed by freeze-drying. The chemical shifts of the two methylene resonances of TPA (15.7 and 60.0 ppm) are similar to those observed for free TPA (TPABr), but the upfield shift of the methyl resonance (11.1 ppm) indicates that there is an interaction between TPA and other species in the synthesis mixture. Upon heating of the synthesis gel and the subsequent appearance of crystalline Si-ZSM-5 by XRD, the characteristic resonances of TPA occluded in Si-ZSM-5 are observed.

Silylation. The sample collected by silylation of the unheated, TEOS-containing synthesis mixture is amorphous by XRD (not shown). However, the IR spectrum contains the vibrational signature of Si-ZSM-5 at 561 cm^{-1} in addition to the Si-O bending mode at 458 cm^{-1} (Figure 9). The bands at 847 and 1254 cm^{-1} correspond to Si- CH_3 modes of the trimethylsilyl groups.²¹ The ^{29}Si MAS and ^1H - ^{29}Si CP MAS NMR spectra each contain four peaks (Figure 10). The resonances at -92, -101, and -112 ppm are assigned to Q^2 , Q^3 , and Q^4 species, respectively. The resonance at 13 ppm corresponds to the trimethylsilyl groups. The observed enhancement of the resonances of the nonsilylated as well as the silylated species by CP suggests that the silicon-containing species are in close contact with

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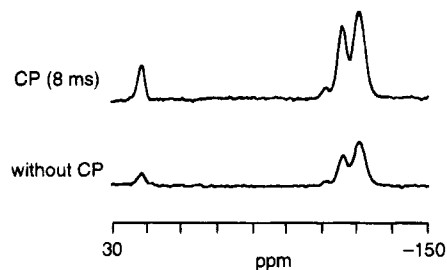


Figure 10. ^{29}Si MAS and ^1H - ^{29}Si CP MAS NMR spectra of the sample collected by trimethylsilylation of the unheated, TEOS-containing synthesis mixture (CP contact time as indicated).

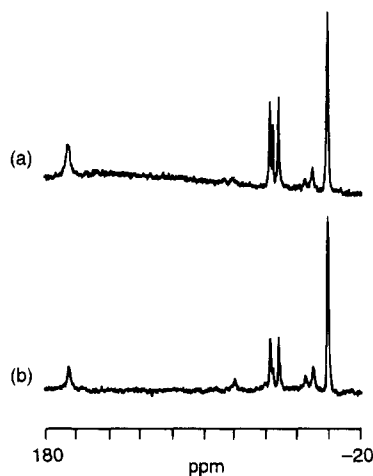


Figure 11. ^1H -decoupled ^{13}C MAS (a) and ^1H - ^{13}C CP MAS (b) NMR spectra of the sample collected by trimethylsilylation of the unheated, TEOS-containing synthesis mixture.

organic protons, similar to the case observed at early stages during the TPA-mediated synthesis of Si-ZSM-5 as well as for crystalline, TPA-containing Si-ZSM-5.

The ^1H -decoupled ^{13}C MAS and ^1H - ^{13}C CP MAS NMR spectra of the silylated product indicate the presence of several organic species (Figure 11). The resonance at 1.3 ppm corresponds to the trimethylsilyl groups. The resonances at 32.2, 35.7, and 37.6 ppm (methyl groups) and at 165.6 ppm (carbonyl) indicate the presence of residual DMF solvent from the silylation procedure. The ^1H - ^{13}C CP MAS NMR spectrum of DMF adsorbed on fumed silica (not shown) exhibits two methyl resonances (32.2, 37.6 ppm) due to the inequivalence of the two methyl groups in the solid state; the third peak (35.7 ppm) in the spectrum of the silylated sample is assigned to more mobile DMF molecules in which the two methyl groups are chemically equivalent (35.2 ppm for DMF in solution). Finally, the resonances at 10.8, 15.6, and 59.9 ppm correspond to TPA. The chemical shift of the methyl resonance indicates that TPA does not experience the geometric constraints and van der Waals interactions that would be present if the channel intersections of Si-ZSM-5 were fully formed. However, the upfield shift of the TPA methyl resonance for this sample relative to that of free TPA suggests that there are van der Waals interactions between TPA and other species in the silylated sample.

In the TGA of the silylated sample, the rate of weight loss is fairly constant (25 wt % total) during heating to 600 °C, and it is difficult to distinguish different stages of desorption and combustion of the various components. The molar compositions indicated by elemental analysis,

Table 1. Molar Composition of the Sample Obtained by Trimethylsilylation

technique	composition				
elemental analysis	mol %				
	C	H	N	Si	O
	9.7	38.3	1.8	13.5	36.7
^{29}Si MAS NMR	mol %				
	$\text{Si}(\text{CH}_3)_3$	Q^2	Q^3	Q^4	
	11.2	4.9	31.0	52.9	
^{13}C MAS NMR	mol % (vs total C content)				
	TPA	$\text{Si}(\text{CH}_3)_3$		DMF	
	4	42		54	

^{29}Si MAS NMR, and ^{13}C MAS NMR are presented in Table 1. On the basis of these results, one estimate of the composition of the precipitate obtained from the silylation procedure is 1TPA:76SiO₂:9.6TMS:6.8DMF:25H₂O. This is a tentative approximation because the various techniques for assessing the product composition do not give mutually consistent results. Nevertheless, this estimate is valuable because in combination with spectroscopic data it suggests that the silylated precipitate is a complex mixture of species, including amorphous silica and silicon-containing species that are in close contact with organic molecules.

Attempts to isolate the individual components of the silylated product were slightly successful. ^1H NMR of the species that are soluble in organic solvents such as chloroform-*d*, methylene-*d*₂ chloride, benzene-*d*₆, or dimethyl-*d*₆ sulfoxide suggested the presence of TPA (0.9 ppm (t), 1.6 ppm (m), 3.1 ppm (m)), DMF (2.9 ppm (s), 3.0 ppm (s), 8.05 ppm (s)), and trimethylsilyl groups (0.1–0.2 ppm (s)) in addition to other, unidentified species. However, these spectra did not provide any additional information. Solution phase ^{13}C and ^{29}Si NMR were also not informative due to the low sensitivities of these nuclei and the low concentration of soluble species. Mass spectrometry of the chloroform-soluble species confirmed the presence of TPA but did not clearly indicate the presence of volatile, ionizable, high molecular weight components such as the proposed inorganic-organic composite species.

Discussion

In a previous study, a mechanism of structure direction in the TPA-mediated synthesis of Si-ZSM-5 was proposed based on the results of ^1H - ^{29}Si CP MAS NMR.¹ The NMR data suggested that upon heating of the synthesis gel, close contact between the protons of TPA and the silicon atoms of the inorganic phase, *i.e.*, on the order of van der Waals interactions, 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. The present work provides additional insight into the nature and occurrence of these composite species.

In this study, sodium has been eliminated from the synthesis mixture. The rates of nucleation and crystallization are slowed in the absence of sodium when a condensed silica source (Cab-O-Sil) is used. However, the presence or absence of sodium does not appear to influence the nature of the interactions between the organic and inorganic components since the ^1H - ^{29}Si CP

MAS NMR profiles are qualitatively similar. In both cases, polarization transfer between the organic protons and the silicate species does not occur in the unheated gels. At this stage, the TPA molecules can only interact with the surface of the particles of condensed silica, and thus a sufficient number of intermolecular contacts for CP to be observed are not established. The silica depolymerizes upon heating of the synthesis mixture, and reorganization of the silicate oligomers occurs such that favorable van der Waals contacts are established between the hydrophobic silicate species and TPA molecules. The observation of efficient ^1H - ^{29}Si CP in the X-ray amorphous, heated samples suggests that restructuring of the silica has occurred and that the inorganic-organic composite species that are thought to be necessary for nucleation have been formed. The observed ^1H - ^{29}Si polarization transfer is not due to the presence of H_2O as an impurity that may have been introduced into the sample during sample preparation since samples prepared using H_2O rather than D_2O demonstrate markedly less-efficient cross polarization. The change in the distribution of Q^3 and Q^4 species in the ^{29}Si MAS NMR spectra also provides evidence that reorganization of the silica has occurred. The presence of sodium may increase the rate at which the depolymerization of silica occurs, thus accelerating nucleation and crystallization. However, it does not appear to affect the nature of the silicate-TPA interactions or, by extension, the mechanism by which structure direction occurs. When sodium is absent, the delay in nucleation may be because there is a threshold concentration or size of the inorganic-organic composite species that must be formed in order for nucleation to occur. It is apparent by ^1H - ^{29}Si CP MAS NMR that there are at least some of these species present after heating the sodium-free synthesis gel for 1 day; the CP profile resembles that for the case in which sodium is present. After crystal growth has begun, a similar correlation between the efficiency of CP and the amount of crystalline material present by XRD is observed for the syntheses in the presence or absence of sodium.

When a readily hydrolyzed, monomeric silica source such as TEOS is used, association of silicate species with the organic structure-directing agent is possible in the unheated synthesis mixture. This is suggested by the occurrence of efficient ^1H - ^{29}Si CP in the freeze-dried sample of the unheated, TEOS-containing synthesis mixture. The observed signal cannot be due to polarization transfer from ethanol that is produced by hydrolysis of TEOS because the ethanol is removed during the process of freeze-drying and is not observed in the ^1H - ^{13}C CP MAS NMR spectrum. The ^1H - ^{13}C CP MAS NMR spectrum also indicates that TPA is present in the solid silicate phase, even after washing with H_2O . The presence of a distinct vibrational band at 560 cm^{-1} in the IR spectrum of the freeze-dried, unheated gel indicates that the silicate ordering in some way resembles that found in crystalline Si-ZSM-5,^{9,10} although no long-range order is apparent by XRD; the 550 - 560 cm^{-1} band is absent from the IR spectrum of neat TEOS or of a freeze-dried sample of TEOS hydrolyzed in the presence of an inorganic base. Thus, inorganic-organic composite species are apparently formed as soon as there is a sufficient amount of soluble silicate present in the synthesis mixture.

The striking efficiency of polarization transfer observed in the Cab-O-Sil-containing samples collected after one day of heating or the unheated, TEOS-containing gel suggests that there is a significant degree of interaction between the TPA molecules and the silicate species in the synthesis mixture at early stages of structure formation. This observation is consistent with the previously proposed mechanism of structure direction by TPA in the synthesis of Si-ZSM-5; that is, the TPA molecules interact with the silicate species and organize them into inorganic-organic composite structures that are ultimately incorporated into the channel intersections of the zeolite product.¹ The propyl chains of TPA may interact preferentially with the hydrophobic silicate species at an appropriate van der Waals contact distance rather than with bulk water.²² Also, there may be a weak electrostatic attraction between the organic cation and the Q^3 sites, as evidenced by the more rapid polarization of the Q^3 sites relative to Q^4 sites at short CP contact times. It thus appears that the TPA molecules are enclathrated into extended silicate structures prior to the appearance of long-range, crystalline order. This process may be related to the formation of cagelike water structures around tetraalkylammonium cations such as TPA due to hydrophobic hydration.²³⁻²⁵ Favorable van der Waals interactions between organic species and hydrophobic silica Q^4 sites have been suggested as the primary thermodynamic driving force for the organic-mediated self-assembly of pure-silica zeolites.^{22,26}

Additional information regarding the conformation of the TPA molecules during the synthesis of Si-ZSM-5 was sought via ^1H - ^{13}C CP MAS NMR. The observed upfield shift and splitting of the methyl resonance relative to that of TPABr are characteristic of TPA located at the channel intersections of Si-ZSM-5. Upon washing to remove free TPA, the samples collected from the unheated, TEOS-containing synthesis gel and from the Cab-O-Sil-based synthesis after 1 day of heating (amorphous by XRD and IR spectroscopy) contain TPA. In all cases, the environment experienced by the TPA molecules within these samples does not exactly resemble that of the channel intersections in crystalline Si-ZSM-5, as suggested by ^1H - ^{13}C CP MAS NMR. The upfield shift of the methyl resonance of TPA relative to its position in the spectrum of TPABr suggests that TPA molecules in these amorphous samples experience additional van der Waals interactions, most likely with silicate species. However, the chemical shift of the methylene carbon adjacent to the nitrogen is unchanged relative to that of free TPA. Thus, the self-assembled structures that appear to be involved in the synthesis of Si-ZSM-5 are composed of TPA and silicate; they are related to but do not have the same rigid geometry as the channel intersections of the product. The final structure is apparently determined as the composite species assemble into Si-ZSM-5. The involvement of extended structures in the TPA-mediated synthesis of

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Si-ZSM-5 is also suggested by small-angle neutron scattering²⁷ and small-angle X-ray scattering data.²⁸

Although isolation of well-defined inorganic-organic composite species from the unheated, TEOS-based synthesis mixture via the silylation technique was not achieved, characterization of the product thus obtained provided observations that are consistent with previous conclusions regarding the nature of the composite species. Enhancement of all of the Si resonances by ^1H - ^{29}Si polarization transfer (despite the presence of H_2O , which can decrease the efficiency of CP) suggests that the organic and inorganic components are in close proximity. ^{13}C MAS NMR indicates that TPA is present in the solid and that the methyl groups experience a constrained environment (van der Waals interactions). However, the environment does not exactly resemble that of the channel intersections in Si-ZSM-5. The organization of silicate units bears some resemblance to that found in Si-ZSM-5, as suggested by the presence of the characteristic vibrational band at 560 cm^{-1} , although the material does not exhibit any long-range order by XRD. The estimated molar composition of the solid phase suggests that even if the composite species have the idealized ratio of silicon to TPA that would be expected from the composition of as-synthesized, crystalline Si-ZSM-5 (Si/TPA = 24), amorphous silica must also be present in the solid sample collected by silylation. Thus, the results of the silylation studies are consistent with previous conclusions regarding the presence of inorganic-organic composite species in the synthesis of Si-ZSM-5.

Proposed Mechanism

The present studies provide additional evidence for the mechanism of structure direction (not pore filling) and self-assembly proposed for the TPA-mediated synthesis of Si-ZSM-5 (Figure 12). The key step in the synthesis of Si-ZSM-5 is the formation of inorganic-organic composite species that then provide the fundamental units for nucleation and crystal growth, as suggested by ^1H - ^{29}Si CP MAS NMR. In essence, the hydrophobic hydration sphere that is formed around TPA in aqueous solution is partially or completely replaced by silica²⁹ when a sufficient amount of soluble silicate species is available. Favorable van der Waals contacts between the alkyl chains of the organic species and the hydrophobic silicate species likely provide the enthalpic driving force for this process, with perhaps an entropic contribution arising from the release of the ordered water molecules from the hydrophobic hydration sphere into bulk water.²⁶ It is through these van der Waals interactions that the geometric correspondence between the structure-directing agent and the zeolite pore architecture that is the hallmark of structure direction arises.²² 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 small amounts

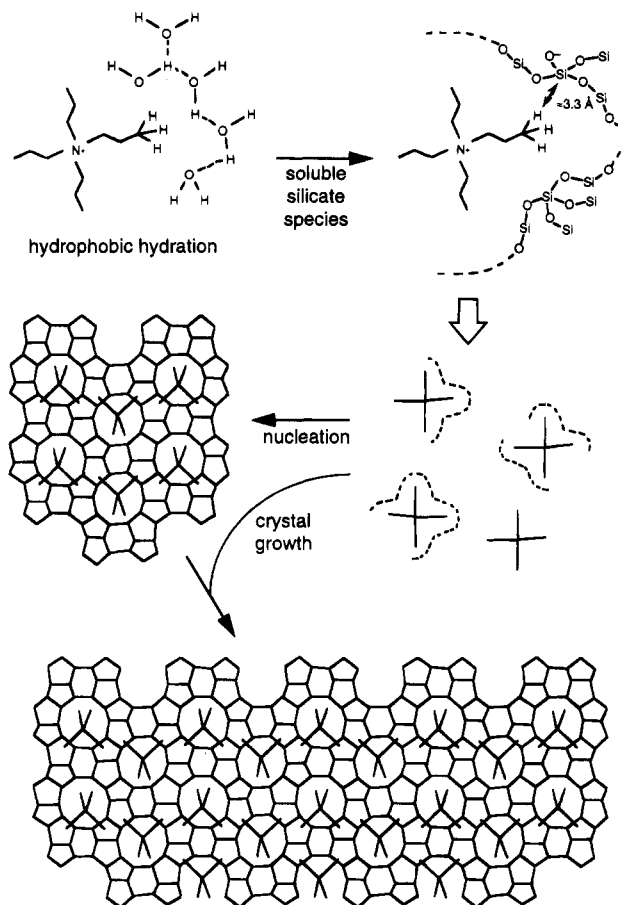


Figure 12. Proposed mechanism of structure direction and crystal growth involving inorganic-organic composite species in the TPA-mediated synthesis of Si-ZSM-5.

of sodium¹ in the synthesis mixture to facilitate dissolution of a condensed silica precursor leads to an enhanced rate of nucleation (at high sodium concentrations the structure-directing influence of sodium is predominant; the formation of layered silicates with a large proportion of anionic Q^3 sites is favored,^{26,30} and the structure-directing tendency of the organic species is no longer observed).

Aggregation of the preformed inorganic-organic composite species is likely responsible for nucleation; this process may occur in solution or on the surface of silica particles³¹ or the walls of the reaction vessel (heterogeneous nucleation). Subsequent crystal growth can occur in a layer-by-layer fashion,¹ as suggested by the layered structure of ZSM-5/ZSM-11 intergrowths³² and other high-silica zeolites.³³⁻³⁵ The observation that tetramethylammonium (TMA) and tetraethylammonium (TEA) can be occluded into aluminosilicate ZSM-5 if the gel contains a sufficient amount of TPA to induce nucleation and sustain crystal growth (Si/TPA = 35;

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TPA/TMA > 1)³⁶ suggests, however, that the composite species may not be the sole component in the crystal growth phase of Si-ZSM-5 (TMA and TEA do not organize silica to form inorganic-organic composite species). Free TPA molecules and silicate species may also be able to diffuse to the surface of the growing zeolite crystal and be incorporated into the crystalline structure. Nevertheless, formation of the inorganic-organic composite species appears to be the key factor in structure direction.

The results described here provide additional evidence for the existence of specific, intermolecular interactions within preorganized inorganic-organic composite structures during the synthesis of Si-ZSM-5.¹ It is through these van der Waals interactions that the geometric correspondence between the structure-directing agent and the zeolite pore architecture that is characteristic of structure direction arises.²² Thus, the detection of interactions between the organic structure-directing

agent and silicate species has broad implications for the design and synthesis of new molecular sieve materials. It suggests that structure direction in zeolite synthesis can be approached in terms of hydrophobic hydration and weak, noncovalent intermolecular interactions. The structural features of the product can perhaps be controlled through the judicious choice of an organic species that can interact with the silicate species in a specific manner as determined by an optimization of van der Waals interactions. The technique of intermolecular cross polarization can be used to further probe these structure-directing interactions.

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