Layered Intermediates in Zeolite Synthesis: Are Structures Related?

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Layered organic−inorganic compounds have been found during the crystallization of zeolites ZSM-48 and beta with hexamethonium and tetraethylammonium cations, respectively. These materials are obtained from gels with relatively high concentrations in organic species but are not stable under hydrothermal conditions. While highly crystalline solids are formed after short synthesis periods, their structure gradually collapses with synthesis time until a completely amorphous compound is formed. The stability of these materials can be increased by lowering the synthesis temperature, but zeolites start to crystallize only after the complete degradation of the layered structures. Even though the synthesis conditions, the gel compositions, and the structure of the final zeolite are different, the two layered materials seem to possess very similar structures, the main difference resulting from the nature of the interlayer organic molecules. These intermediate compounds display interesting intercalation properties toward long alkylammonium cations. Silica layers can be swollen at low temperature without any modification of their crystallinity. Spectroscopic characterization of the materials as well as their evolution over the whole crystallization period tends to indicate that zeolites are not formed via layered intermediates, as was previously claimed. Actually, these solids only provide the synthesis medium with silicate and aluminosilicate species necessary for the crystallization of the zeolite, whose structure is directed by the organic species present in the solution.

Introduction

Hydrothermal treatments of precursor gels containing a silica (or an aluminosilicate) source, organic molecules, and water at temperatures in the range 100−200 °C often lead to the formation of crystalline materials. These materials can possess a three-dimensional (3D) framework of tetrahedra-like zeolites or clathrasils or can be two-dimensional (2D) layered aluminosilicates made of inorganic layers separated by organic molecules. The preferential formation of 2D or 3D networks depends not only on the initial gel composition but also strongly on the crystallization conditions. Indeed, mixtures with a given composition can lead to either zeolites or layered materials when the hydrothermal treatment is performed at different temperatures. As an example, it has been reported that the system SiO_2−piperazine−H_2O could give ZSM-39 (Dodecasil 3C) at 180 °C,[1] ZSM-48 at temperatures between 150 and 180 °C,[2] or the lamellar piperazine−silicate EU-19 in the 120−150 °C temperature range,[3] whose structure is made of silica double layers separated by and hydrogen-bonded to piperazinium ions. Upon calcination in air at 800 °C, EU-19 is converted to the silica polymorph EU-20, probably formed by cross-linking of the silicate layers

at high temperature. Such formation of three-dimensional networks upon calcination of layered precursors has also been recently reported for MCM-22,[4] the borosilicate ERB-1,[5] and PREFER,[6] a precursor of a ferrierite-type zeolite.

In some cases, lamellar compounds are formed prior to the crystallization of a three-dimensional network and have been regarded as precursors of three-dimensional microporous frameworks.[7−9] During the crystallization of zeolite beta with tetraethylammonium (TEA+) cations, Lohse et al.[10] observed that a crystalline layered material was obtained at short synthesis times, while prolonging the crystallization period led to the formation of pure zeolite beta. From these observations, the authors concluded that zeolite beta is formed via a layered aluminosilicate, by direct transformation of the latter to a three-dimensional framework. However, in the absence of data concerning the evolution of the

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system over the whole crystallization period, such a conclusion is more than questionable.

The present paper reports on the synthesis and characterization of two layered silicates obtained during the crystallization of ZSM-48 with hexamethonium ions and zeolite beta with tetraethylammonium cations. These two preparations have been chosen because of the relatively high stability of the layered compounds under synthesis conditions. Moreover, even though gel compositions, crystallization conditions, and the nature of the final zeolite formed are completely different, the layered material seems to possess very similar structures. The complete transformation of these materials to zeolites has been monitored by numerous techniques, principally X-ray diffraction and solid-state nuclear magnetic resonance (NMR). The aim of this study was to characterize the layered materials and their evolution with time in order to answer, at least partially, the fundamental question: "Are layered materials really precursors of zeolites; i.e., are the latter formed by direct transformation of two-dimensional crystalline structures under synthesis conditions?".

Experimental Section

Synthesis. Layered hexamethonium silicates (HM-silicates) were prepared by hydrothermal crystallization of gels containing silica, hexamethonium (hexamethylenebis(trimethylammonium)) hydroxide (HM(OH)$_2$), and water. In a typical preparation, tetraethyl orthosilicate (TEOS, Aldrich) or amorphous silica (A 200, Degussa) was hydrolyzed with an aqueous molar solution of HM(OH)$_2$ under vigorous stirring at room temperature for about 1 h. Water was then added, and stirring was maintained for 0.5 h. When TEOS was used as silica source, the resulting mixture was heated at 80 °C for ca. 3 h to remove ethanol formed upon hydrolysis of the alkoxide. The gel, with the following composition

$$SiO_2 - 0.2 \; HM(OH)_2 - 30 \; H_2O$$

was then transferred into a Teflon-lined stainless steel autoclave and heated under stirring (60 rpm) at temperatures between 100 and 180 °C for various periods.

A HM-aluminosilicate material was also prepared following the previous recipe by adding aluminum (Al(NO$_3$)$_3$·9H$_2$O) to the precursor gel (Si/Al = 100).

The lamellar tetraethylammonium aluminosilicate (TEA aluminosilicate) was prepared using an amorphous SiO$_2$–Al$_2$O$_3$ cogel (Si/Al = 100), tetraethylammonium hydroxide (TEAOH, 25 wt % in water, Aldrich), and water. The SiO$_2$–Al$_2$O$_3$ cogel was obtained by hydrolysis of TEOS and aluminum isopropoxide in a dilute hydrochloric solution (0.1 N) followed by addition of TEAOH until precipitation of the gel and finally drying at 110 °C for 12 h. The dry gel was then dispersed in an aqueous solution of TEAOH under stirring, and the resulting mixture with the composition SiO$_2$–0.005 Al$_2$O$_3$–0.45 TEAOH–5.8 H$_2$O was heated under stirring (60 rpm) at 135 °C for 2–10 days.

For both syntheses, solids were recovered by centrifugation, washed with distilled water, and air-dried at room temperature.

For comparison, a sample of piperazine–silicate–EU-19 was also synthesized following a literature procedure.[3]

Characterization. X-ray powder diffraction patterns of the lamellar compounds were recorded on a Philips PW 1710 diffractometer (Cu Kα radiation) from 1° to 50° (2θ) in 0.02° steps with 1 s per step. SiO$_2$ was used as an external standard. The crystallinity of the materials was estimated by comparing the relative intensities of the basal reflections in the X-ray powder patterns. Framework infrared spectra were collected on a Vector 22 FTIR spectrometer (Bruker) using KBr wafers
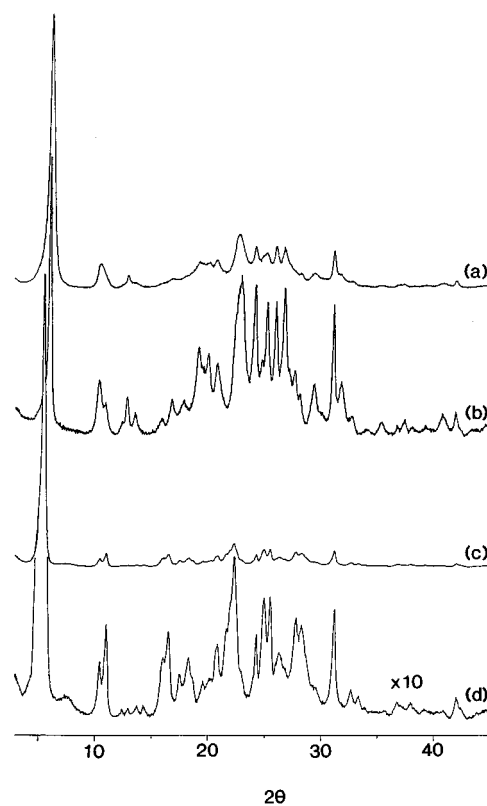
Figure 1. X-ray diffraction patterns of HM-silicate prepared at 180 °C (a) and 150 °C (b) and of the TEA-layered compound obtained at 135 °C (c, d).

(1 wt % solid in KBr). SEM pictures have been obtained with a Hitachi S 800 microscope. Thermal analysis data were recorded on a Setaram TG/DSC 111 apparatus. Samples were heated from 25 to 800 °C in an air flow at a heating rate of 10 °C/min.

Solid-state NMR spectra were acquired on a Bruker DSX 400 spectrometer equipped with a 4 mm double-bearing probe head. All ^{1}H–^{29}Si CP/MAS spectra were recorded with a standard cross-polarization sequence at a spinning speed of 5 kHz. The contact time was varied from 150 μs to 30 ms, and the recycle delay between consecutive scans was 10 s.^{29}Si MAS spectra were obtained with high-power proton decoupling and 60 s recycle delay to allow a complete relaxation of all silicon species. ^{29}Si chemical shifts were referenced to tetramethylsilane (TMS).

Intercalation of organic molecules in the layered compounds was achieved by reacting 1 g of the dry solid with 100 mL of an aqueous solution of the corresponding molecule at 80 °C under stirring for various periods. The solid was then recovered by centrifugation, washed with distilled water, and air-dried at room temperature.

The amount of aluminum in the samples was measured by ICP after solubilization of the solids in HF:HCl solutions.

Results and Discussion

Synthesis. The first HM-silicate material was prepared by heating a gel at 180 °C under stirring, which are the typical conditions for the crystallization of pure silica ZSM-48.[11] After 5 days, a highly crystalline ZSM-48 zeolite is effectively obtained, as evidenced by X-ray diffraction. However, when the crystallization process is interrupted after 55 h, a different material is formed, characterized by an intense reflection at low θ values (2θ = 6.2°) in the X-ray pattern (Figure 1). The pattern is characteristic of a layered silicate structure with a strong basal spacing peak. Comparison of interplanar
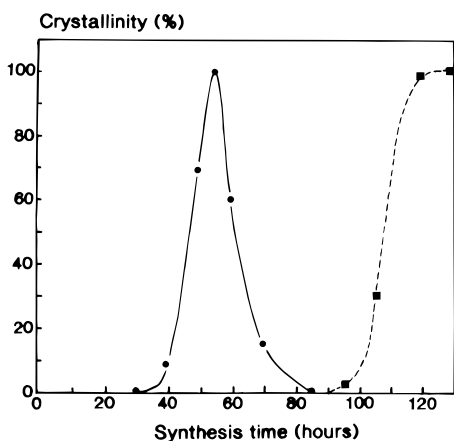
Figure 2. Evolution of the crystallinity of HM-silicate (●) and pure silica ZSM-48 (■) with synthesis time at 180 °C.

d spacings with literature data indicated that the material was similar to the layered hexamethonium silicate HMEU-3, first reported in 1982.[12] Syntheses performed with crystallization periods comprised between 30 and 120 h revealed that the HM-silicate is only obtained within a very short crystallization time interval centered around 55 h. Prolonging the synthesis period results in a decrease of the crystallinity of HM-silicate, as evidenced by a decrease of the intensity of the basal X-ray reflection, until a completely amorphous solid is obtained at ca. 96 h. After 100 h, new reflections appear in the X-ray pattern, which indicates the formation of pure silica ZSM-48. Figure 2, which reports the evolution of the crystallinity of HM-silicate and ZSM-48 as a function of the synthesis time, clearly shows that the two materials never coexist during the hydrothermal process. For HM-layered silicates, the crystallinity was normalized with respect to that of the sample obtained after 55 h.

The highly crystalline HM-silicate is in the form of aggregated platelets with individual crystals of ca. 1−3 μm length and less than 0.1 μm thickness, whose morphology is characteristic of two-dimensional layered structures (Figure 3). Increasing the crystallization time from 55 to 96 h results in a modification of the crystals size and morphology. At 60 h, crystals still possess a platelike morphology, but bulges are observed at the periphery. These bulges grow with synthesis time, the transformation being complete at ca. 96 h. The corresponding amorphous solid is in the form of small shapeless particles. Finally, the solid recrystallizes, and needles typical of zeolite ZSM-48 are observed after 120 h. A ^{13}C NMR examination of the liquid phase obtained after centrifugation of the zeolite revealed the presence of significant amounts of trimethylamine, most probably formed by Hofmann's degradation of quaternary ammonium cations, which is known to occur at relatively high temperatures. As a consequence, the concentration of HM^{2+} cations in the synthesis medium decreases with crystallization time. After degradation, organic molecules are probably expelled from the solid, which explains the formation of humps at the periphery of the crystals and the gradual destruction of the layered structure. Note that thermal analysis data indicated that HM-silicate contains 20 wt % of organics, which corresponds to approximately 50% of HM^{2+} cations originally introduced in the precursor gel. After 96 h of

crystallization, the amount of organic molecules occluded in the completely amorphous solid phase has decreased to 0.3 wt %. However, even after 4 days at 180 °C, the HM^{2+} concentration in the liquid phase is high enough to allow the crystallization of ZSM-48, which is usually performed with $HM^{2+}/SiO_2 \approx 0.05$.[13] A ^{13}C CP/MAS NMR spectrum of the zeolite showed that only HM^{2+} species are occluded in the channels and that products of the degradation of the latter do not act as templating molecules.

These results suggest that the crystallization of HM-silicate and ZSM-48 require different gel compositions, in particular different HM^{2+}/SiO_2 ratios. High ratios favor the formation of the layered material whereas low ratios preferentially lead to the crystallization of the zeolite. Indeed, ZSM-48 could be directly obtained after 48 h at 180 °C when the synthesis was performed with $HM^{2+}/SiO_2 = 0.05$ in the precursor gel, and intermediate layered compounds were not observed.

The major problem encountered during the crystallization of the layered HM-silicate at high temperature is the lack of stability of the material under hydrothermal conditions, which makes difficult the reproducible preparation of highly crystalline solids. A possibility to increase the stability of HM-silicate is to decrease the rate of quaternary ammonium cations degradation by lowering the synthesis temperature. Moreover, low temperatures may considerably inhibit the crystallization of ZSM-48, which requires temperatures higher than 170 °C. A series of syntheses have been carried out using a gel with the composition given in the Experimental Section at temperatures ranging from 100 to 150 °C. For all temperatures a solid phase was formed after 3 days, whose XRD pattern is similar to that of HM-silicate prepared at 180 °C, indicating that the layered material can be formed within a quite broad temperature range. However, differences in XRD peak intensities are observed, principally for the basal reflection at $2\theta = 6.2°$, whose intensity decreases at low temperatures. Since the intensity of the other reflections do not significantly change with temperature, this probably reflects a modification of the crystals morphology. At 180 °C, relatively large platelets were formed, and preferential orientation of the latter under the X-ray beam explains the high intensity of the basal reflection. At lower temperatures, individual crystals are smaller and stick together to form round-shaped aggregates (Figure 3). On the basis of X-ray line width and resolution of the pattern, the crystallinity of HM-silicate was maximum when the synthesis was performed at 150 °C.

The layered structure can also be obtained using amorphous silica A 200 instead of TEOS as silicon source. For zeolites, the use of polymeric silica sources usually decreases the rate of crystallization as compared to the case of TEOS and leads to the formation of larger individual crystals.[14] In the present case, crystals were not significantly different from those obtained with

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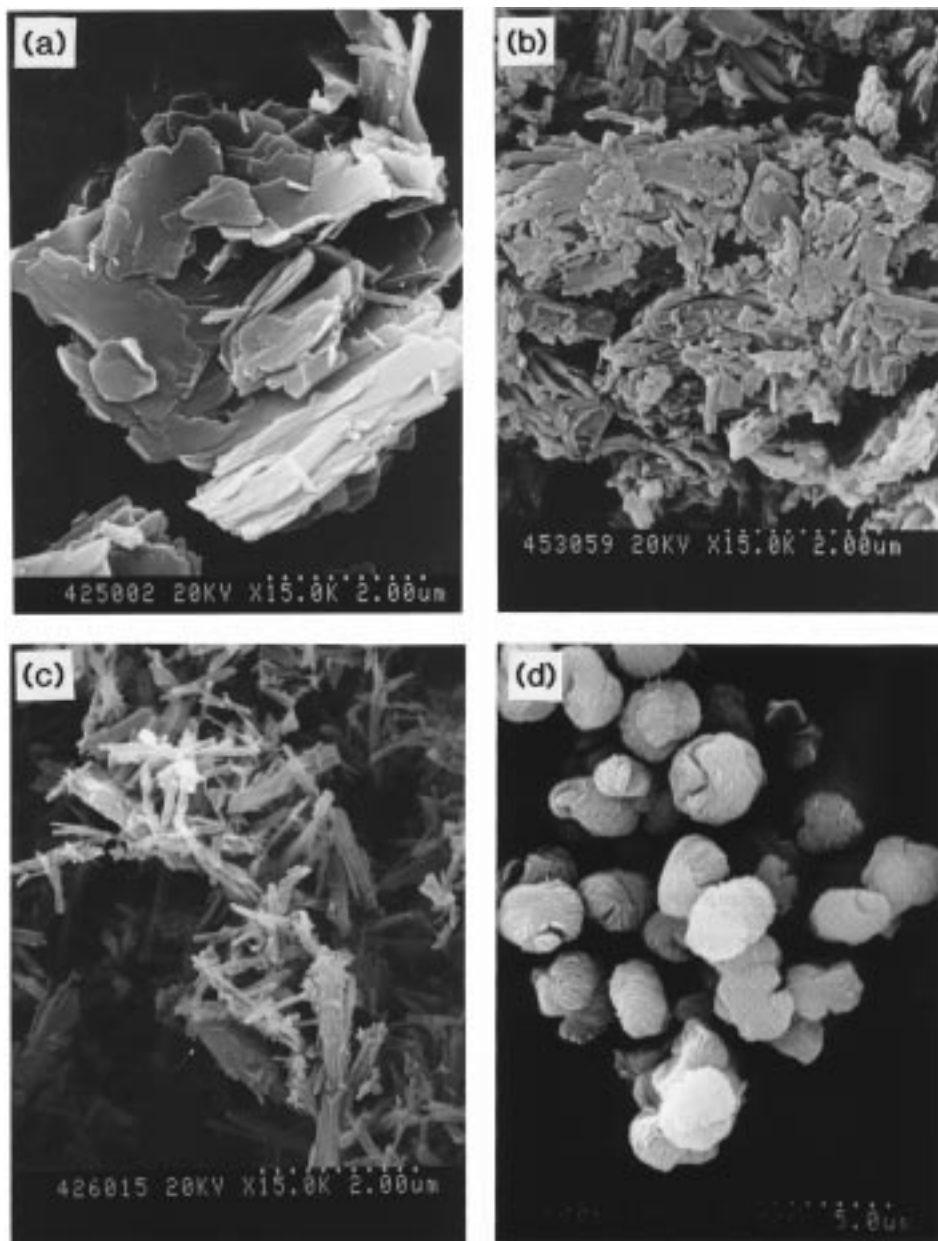
Figure 3. SEM pictures of the solid phase obtained during the crystallization of ZSM-48 and recovered after 55 (a), 65 (b), and 120 h (c). Picture (d) corresponds to the HM-layered compound obtained at 150 °C for 3 days.

TEOS, and X-ray diffraction showed that the crystallinity of the sample was even increased. Some of the reflections that were quite broad on samples prepared with TEOS were better resolved (Figure 1).

The kinetics of crystallization as well as the stability of HM-silicate at 150 °C have been studied by recovering the solid phase after 3, 6, and 10 days of hydrothermal treatment. Basically, no significant modifications in the X-ray pattern are observed when the synthesis period is increased from 3 to 6 or 10 days. This indicates that the layered material is stable at 150 °C under hydrothermal conditions, which was not the case at 180 °C. Moreover, some of the X-ray reflections are better resolved after 10 days, suggesting that the crystallinity of HM-silicate increases with the synthesis time.

Syntheses performed with TEA$^+$ cations at 135 °C also led to the crystallization of layered materials after 2 days. The X-ray powder pattern of the TEA aluminosilicate is also characteristic of a layered structure with a very strong basal reflection at $2\theta = 5.4°$ (Figure 1). The resolution of the pattern is high compared to that previously reported by Lohse et al.,[10] particularly in the region corresponding to 2θ values between 15° and 40°. However, the similarity between the two diffractograms indicates that we have prepared the same material. No modifications were observed when the crystallization time was increased to 4 days. However, reflections typical of beta zeolite appeared after 10 days, and the zeolite was fully crystallized after 15 days. Experiments performed by collecting the solid phase after different crystallization periods showed a complete degradation of the TEA-layered structure prior to beta zeolite crystallization. As previously observed for the HM-silicate, this strongly suggests that the zeolite is not formed via a direct transformation of the layered material but rather by a slow redissolution of an amorphous $SiO_2-Al_2O_3$ precursor in basic medium. This was also confirmed by analyzing the modification of the
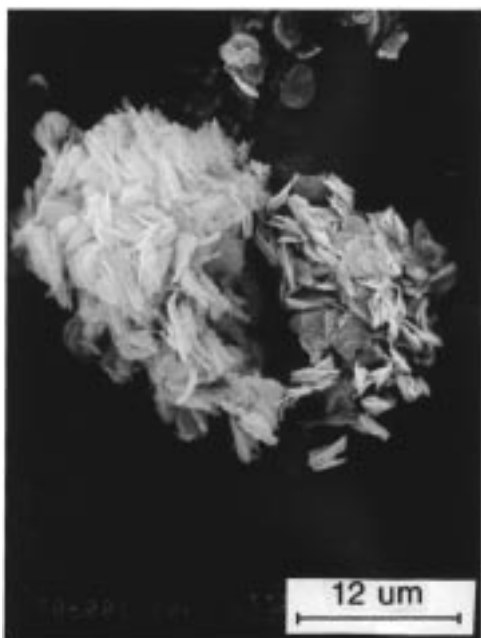
Figure 4. Typical morphology of the TEA-layered compound obtained at 135 °C for 4 days.

particles morphology as evidenced by SEM. The TEA aluminosilicate is in the form of small platelets aggregated together to form particles of ca. 10−20 μm (Figure 4). After 8 days, the solid phase is completely amorphous and crystalline morphologies are no longer observed. Finally, zeolite beta shows very small individual crystals of ca. 0.2 μm diameter forming agglomerates with nonuniform dimensions comprised between 2 and 30 μm. Therefore, it was not possible from SEM pictures to find any relationship between the morphology of zeolite crystals and that of the layered material particles.

Characterization. On the basis of synthesis results, a sample of HM-silicate has been prepared at 150 °C for 10 days using A 200 as silicon source and characterized by various techniques. The TEA-layered compound was obtained at 135 °C after a crystallization period of 4 days.

X-ray Diffraction. As already mentioned, XRD patterns of both HM and TEA-layered materials are characterized by the presence of a low angle reflection at 6.2° and 5.4° (2θ), respectively (Figure 1). The patterns show sharp and relatively broad reflections simultaneously, suggesting that the solids do not possess a long-range order in all three dimensions. Because of the presence of broad X-ray peaks, attempts to estimate the unit cell parameters and to index the patterns were unsuccessful. Assuming that these materials are made of regular silica layers separated by organic molecules, it is possible to estimate the thickness of inorganic layers (WT) from the d-spacing values corresponding to the basal reflection using the relation $d = WT + GH$, where GH is the gallery height, corresponding approximately to the size of the organic molecule. These values are 14.1 and 16 Å for HM and TEA-layered materials, respectively. Considering the dimensions of HM^{2+} cations (approximately 16 Å length and 7 Å diameter for the headgroups),[13] it is unlikely that the latter be oriented perpendicularly to the silicate layers. One possibility is that organic molecules stand
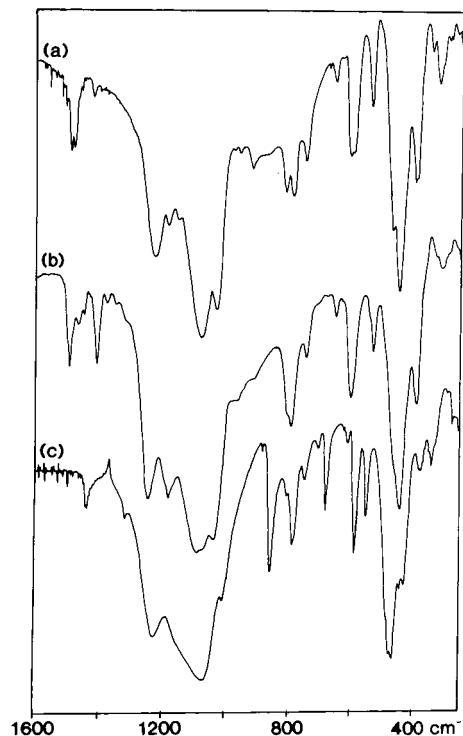
Figure 5. Framework infrared spectra of HM (a), TEA (b), and EU-19 (c) layered materials.

parallel to the layers which leads to a thickness of approximately 7.2 Å for the latter. A very close value (7.1 Å) can be found for the TEA-layered compound. Taking an average value of 2.9 Å for Si−O−Si bond lengths (calculated from the structure of EU-19),[15] both structures could be represented as silicate (or aluminosilicate) double layers separated by quaternary ammonium cations. Such silica double layers have already been found in the layered materials EU-19, prepared in the presence of piperazine[15] and PREFER.[6]

Infrared Spectroscopy. The framework infrared spectrum of HM-silicate is composed of sharp and well-defined absorption bands (Figure 5). Interpretation of infrared spectra of silicate materials is not trivial even though a tentative assignment of the absorptions has been proposed for zeolites.[16] In particular, interesting information about the arrangement of tetrahedra in zeolites can be derived from the study of IR bands in the 500−650 cm^{-1} region. Indeed, these bands have been assigned to the presence of double rings of tetrahedra in the framework. Infrared vibrations around 1000−1100, 800, and 450 cm^{-1} have been attributed to the Si−O asymmetric stretch, symmetric stretch, and bend, respectively, and are not structure sensitive. By contrast, other vibrations, particularly those between 500 and 650 cm^{-1}, strongly depend on the local arrangement of tetrahedra in the framework and can be considered as a "fingerprint" for a given structure.

The infrared spectrum of the TEA-layered material is very similar to that of HM-silicate. Basically, the same absorption bands are present at the same fre-

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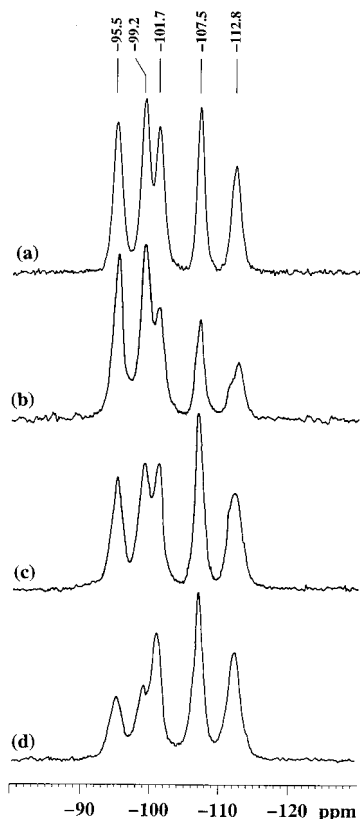
Figure 6. ^{29}Si NMR spectra of HM-silicate: (a) ^{29}Si MAS NMR spectrum; (b–d) ^{1}H–^{29}Si CP/MAS spectra recorded with 150 μs, 5 ms, and 30 ms contact time, respectively.

quencies, and only minor differences can be observed in the region around 800 cm^{-1}. However, as will be reported later, these differences are not significant, since bands around 800 cm^{-1} change with the nature of the organic molecules present in the interlayer space. The fact that HM and TEA-layered silicates possess the same absorption bands over the whole frequency range (300–1500 cm^{-1}) suggests that the arrangement of tetrahedra within inorganic layers is the same for the two materials. As a consequence, HM- and TEA-silicates could be regarded as similar materials, the only difference being the distance between inorganic layers, which is dictated by the size of the organic molecule.

IR spectra of the two materials are different from that of EU-19, whose structure was determined by single-crystal X-ray diffraction using synchrotron radiation.[15] However, common features are observed like a broad absorption band around 1230 cm^{-1}. A similar band has been observed for mesoporous silica MCM-41 and can be unambiguously attributed to Si−O^{-} moieties balancing the positive charge of tetraalkylammonium cations.

Solid-State NMR. Five magnetically nonequivalent silicon species can be observed in the ^{29}Si MAS NMR spectrum of HM-silicate (Figure 6). Deconvolution of the spectrum with Gaussian lines gives relative intensities of 1:1:1:1:1 within experimental error for the five resonances. Two of these peaks at ca. −112.8 and −107.5 ppm/TMS are in the region of Q^4 species and correspond to silicon atoms surrounded by four Si atoms: Si(OSi)$_4$. As the synthesis was performed in the absence of aluminum, the three low field peaks could correspond to Q^3 units. The NMR line width is almost the same for the four peaks between −95 and −108 ppm

Table 1. Cross-Polarization Time Constants $T_{\text{H–Si}}$ and Proton Relaxation Times in the Rotating Frame $T_{1\rho\text{H}}$ for ^{29}Si Signals of HM-Silicate Obtained from Cross-Polarization Experiments

| δ (ppm)	$T_{\text{H–Si}}$ (ms)	$T_{1\rho\text{H}}$ (ms)	δ (ppm)	$T_{\text{H–Si}}$ (ms)	$T_{1\rho\text{H}}$ (ms)
−95.5	1.7	16.0	−107.5	2.8	26.3
−99.2	1.6	17.2	−112.8	3.0	26.1
−101.7	2.3	26.3			

($\Delta \approx 200$ Hz) but is higher for the line at −112.8 ppm, which indicates that this line could be the superposition of several NMR lines with very close chemical shifts. More information about the assignment of ^{29}Si NMR lines can be obtained by using ^{1}H−^{29}Si CP/MAS experiments. It has been widely reported that the time constant $T_{\text{H–Si}}$, which characterizes the efficiency of the magnetization transfer between protons and ^{29}Si nuclei, is relatively short for Q^3 species (Si−OH groups) while it is typically 2 or 3 times longer for Q^4 units.[14] Therefore, ^{29}Si NMR resonances corresponding to Si−OH groups are expected to be exalted at low contact times. This is clearly shown in Figure 6, particularly when comparing spectra obtained with 150 μs and 30 ms contact times. At 150 μs, the most intense peaks are those at −95.5 and −99.2 ppm. Surprisingly, the line at −101.7 ppm has a relatively low intensity. Increasing the contact time results in an increase of relative intensities of resonances at −101.7, −107.5, and −112.8 ppm. For a contact time t_c = 5 ms, the CP/MAS spectrum is similar to that obtained under MAS conditions since this value corresponds to the maximum of the intensity for all resonances. At longer contact times, proton relaxation makes that lines at −95.5 and −99.2 ppm have almost disappeared whereas the others are still present. From the evolution of the NMR intensity with contact time, it is possible to estimate $T_{\text{H–Si}}$ and $T_{1\rho\text{H}}$, the proton relaxation time in the rotating frame, for each of the five silicon species (Table 1). For a given contact time t_c, the ^{29}Si magnetization can be approximated as[17]

$$M(t_c) = M_0(1 - \exp\{-t_c/T_{\text{H–Si}}\}) \exp\{-t_c/T_{1\rho\text{H}}\}$$

where M_0 is proportional to the number of silicon nuclei for the corresponding NMR resonance. As seen in Table 1, $T_{\text{H–Si}}$ values corresponding to signals at −95.5 and −99.2 ppm are significantly lower than the others, thus supporting their assignment as Q^3 species. Nevertheless, the other species also possess relatively short $T_{\text{H–Si}}$ values, which makes that the assignment of the resonance at −101.7 ppm is not trivial. Short $T_{\text{H–Si}}$ values probably result from an indirect magnetization transfer from protons of water and organic molecules to Q^4 species. Another possibility to distinguish between Q^4 and Q^3 species in silicates consists of recording NMR spectra at low spinning speeds. Under such conditions, spinning sidebands are observed, whose envelop gives direct information about the chemical shift anisotropy tensor and, thus, the symmetry of the silicon atom. Q^4 species are expected to be relatively isotropic species with a small chemical shift anisotropy. By contrast, the presence of a Si−OH or Si−O$^-\cdots$R$^+$ bond (where R$^+$ is

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*Intermediates in Zeolite Synthesis*

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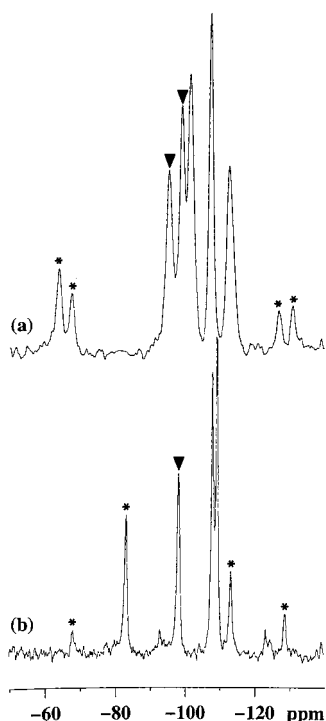
Figure 7. ^{1}H$-^{29}$Si CP/MAS NMR spectra of HM-silicate (a) and EU-19 (b) recorded with spinning speeds of 2500 and 1200 Hz, respectively. Arrows indicate Q^3 sites and asterisks the corresponding spinning sidebands.

an organic cation) modifies the symmetry around silicon species and leads to broad chemical shift tensors with an axial symmetry.

The technique is clearly illustrated in Figure 7 which reports the ^{29}Si CP/MAS NMR spectra of EU-19 recorded at 1.2 kHz. The unit cell of EU-19 contains three nonequivalent silicon sites.[15] Two of them are Q^4 sites while the third one is a Q^3 site balancing the positive charge of piperazinium ions. From chemical shifts values and ^{1}H$-^{29}$Si CP/MAS experiments, NMR lines at -108.4 and -109.7 ppm can be assigned to Q^4 species and the line at -98.6 ppm to Q^3 species. The ^{29}Si NMR spectrum recorded at 1.2 kHz shows that Q^4 sites effectively possess small chemical shift anisotropies while the line at -98.6 ppm gives a broad sideband pattern.

The ^{1}H$-^{29}$Si CP/MAS NMR spectrum of HM-silicate recorded at 2.5 kHz unambiguously demonstrates that lines at -95.5 and -99.2 ppm can be assigned to Q^3 sites but that the resonance at -101.7 ppm corresponds to a Q^4 species (Figure 7). Thus, the structure of HM-silicate contains two nonequivalent Q^3 sites and three nonequivalent Q^4 sites. The Q^3/Q^4 ratio is relatively high (Q^3/Q^4 = 0.67) but is typical of layered silicate structures. Among the two Q^3 sites, it is reasonable to assume that one corresponds to a silanol group Si$-$OH whereas the other is a Si$-$O$^-$ defect that neutralizes the framework charge. On the basis of this assignment, it is possible to propose a chemical composition for the dry solid. Indeed, HM-silicate contains one Si$-$OH group, one Si$-$O$^-$ moiety balancing the charge of 0.5 HM^{2+} cations, and three Si(OSi)$_4$ species. The chemical formula can thus be estimated as

$$Si_2O_3(OH)_2 - Si_2O_5{}^{2-} \cdot HM^{2+} - Si_6O_{12}$$
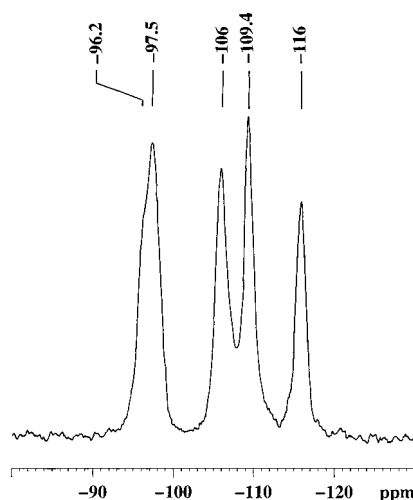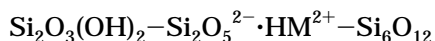
Figure 8. ^{29}Si MAS NMR spectrum of the TEA-layered compound.

or

$$HM^{2+} - Si_{10}O_{20}(OH)_2{}^{2-}$$
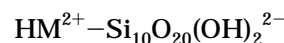
The ^{29}Si MAS NMR spectrum of the TEA-layered material also shows five resonances at -96.2, -97.5, -106, -109.4, and -116 ppm with intensity ratios of 1:1:1:1:1 (Figure 8). This suggests that, as for HM-silicate, the structure contains five nonequivalent tetrahedral sites. The spectrum is very different from that reported by Lohse et al.[10] for the same type of material. NMR spectra recorded with a cross-polarization sequence at various contact times and at low spinning speeds showed that the resonances at -96.2 and -97.5 ppm can be assigned to Q^3 species whereas the three others correspond to Q^4 species. Since the material was prepared in the presence of aluminum, it is possible that one of the lines around -97 ppm also contains the contribution of Si(1Al) species. However, the corresponding intensity is negligible since chemical analysis of the material gave Si/Al = 148.

Thermogravimetric Analysis. The TG and DTG curves recorded upon heating HM-silicate in air show two peaks at ca. 110 and 310 °C. The first one can be attributed to the removal of water molecules and the second to the thermal degradation of hexamethonium cations. These peaks correspond to approximately 6.8 and 22 wt % of the initial amount of material. An additional weight loss is also observed between 500 and 800 °C, which probably corresponds to the removal of water formed by dehydroxylation of the material. X-ray diffraction spectroscopy showed that the material becomes amorphous at 350 °C and is thus not stable upon removal of the organic molecules. The high amount of organic molecules as well as their low degradation temperature is characteristic of a layered structure. Indeed, the decomposition temperature is very close to that of the thermal decomposition of HMBr$_2$. Under similar conditions, the removal of HM^{2+} cations from the channels of zeolite ZSM-48 occurs at ca. 550 °C, i.e., about 250 °C above the decomposition temperature in HM-silicate. FromTG data, it is possible to estimate the composition of the material:

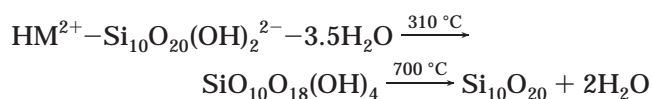$$HM^{2+}/SiO_2 \approx 0.1, \quad H_2O/SiO_2 \approx 0.35$$
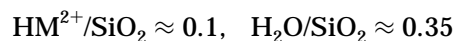
Moreover, assuming that the weight loss observed between 500 and 800 °C corresponds to the dehydroxylation of the material, data indicate the removal of 0.2 H_2O per Si atom in this temperature interval. These water molecules result from the condensation of 0.4 silanol groups. On the basis of these results, the chemical formula for HM-silicate can be estimated as

$$HM^{2+}-Si_{10}O_{20}(OH)_2{}^{2-}-3.5H_2O$$
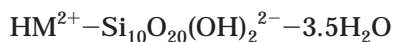
Before calcination, HM-silicate contains only two silanol groups, but two additional groups are formed upon degradation of hexamethonium cations:

$$Si-O^-\text{---}(Me)_3N^+-R \xrightarrow{T} Si-OH$$
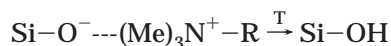
Therefore, the consecutive steps of the thermal evolution of HM-silicate can be represented by the following reactions:

$$HM^{2+}-Si_{10}O_{20}(OH)_2{}^{2-}-3.5H_2O \xrightarrow{310\ °C}$$
$$SiO_{10}O_{18}(OH)_4 \xrightarrow{700\ °C} Si_{10}O_{20} + 2H_2O$$

Thermal analysis data are thus in excellent agreement with NMR data.

For the TEA-layered material, a similar study leads to the following approximated chemical formula:

$$2TEA^+-Si_{10}O_{20}(OH)_2{}^{2-}-2.5H_2O$$

which again agrees with NMR data. On the basis of infrared spectra, we have proposed that HM and TEA-layered materials could possess similar silicate layers and that the main difference between the two materials could result from the nature of the quaternary ammonium cations. Under such conditions, the neutralization of the framework negative charge necessitates that the amount of TEA^+ cations is twice that of HM^{2+} cations, which is effectively observed by thermal analysis.

Intercalation Properties. One of the properties of lamellar materials is their ability to intercalate various organic cations between the layers by chemical exchange. This has been widely used to increase the gallery height of magadiite in order to obtain materials with high surface areas.[18,19] More recently, zeolite MCM-22 was intercalated by cetyltrimethylammonium ($CTMA^+$) cations to prepare MCM-36.[20] Millini et al.[5] have also reported that ERB-1 displayed intercalation properties toward small molecules.

CTMA/HM-silicate has been prepared by reacting HM-silicate with an aqueous solution of cetyltrimethylammonium bromide (CTMABr) at 80 °C for 2 h. Many papers have recently reported that silica species could form mesoporous or lamellar silicates in the presence of $CTMA^+$ cations, the nature of the product formed depending on the gel composition, particularly the $CTMA/SiO_2$ ratio.[18] $CTMA^+$ cations have also been used to swell kanemite and transform it into mesoporous silica MCM-41[19] or to synthesize MCM-36 from $CTMA^+$-intercalated MCM-22.[17]

(18) Dailey, J. S.; Pinnavaia, T. J. *Chem. Mater.* **1992**, *4*, 855.
(19) Sprung, R.; Davis, M. E.; Kaufman, J. S.; Dybowski, C. *Ind. Eng. Chem. Res.* **1990**, *29*, 213.
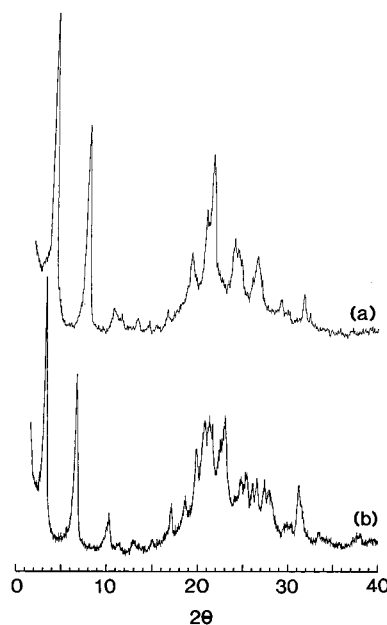
Figure 9. X-ray diffraction patterns of CTMA/HM-silicate after one (a) and four (b) exchanges with an aqueous solution of CTMABr.
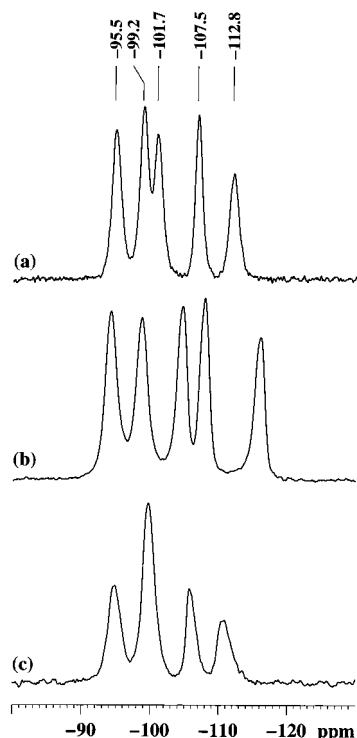
The X-ray diffraction pattern of the intercalated material shows a strong basal reflection at $2\theta = 3.45°$, which demonstrates that $CTMA^+$ cations have effectively modified the distance between silica layers (Figure 9). This reflection corresponds to a d spacing of 25.8 Å. Since the length of $CTMA^+$ cations is approximately 18.5 Å, the value of the d spacing suggests that inorganic layers are separated by monolayers of surfactant molecules. The presence of intense reflections in the 15−35° range indicates that swelling of HM-silicate with $CTMA^+$ cations did not result in an amorphization of silica layers. This was supported by infrared spectroscopy. The framework IR spectrum of CTMA/HM-silicate is very similar to that of the starting material. The crystalline nature of inorganic layers is clearly evidenced by the presence of intense well-defined absorption bands in the region between 300 and 1500 cm^{-1}. By contrast, the ^{29}Si MAS NMR spectrum of the intercalated compound is completely different from that of the starting solid (Figure 10). Five sharp resonances with the same intensity are observed at −94.2, −98.7, −104.7, −107.9, and −116.1 ppm. The line width for each resonance as well as the absence of broad signals between −100 and −120 ppm is an additional indication that the crystallinity of the material was preserved upon intercalation.

A $^1H-^{13}C$ CP/MAS NMR examination of CTMA/HM-silicate revealed the presence of signals characteristic of $CTMA^+$ cations. However, the sharp resonance at ca. 54 ppm, typical of HM^{2+} cations, was still visible on the spectrum of the intercalated material, suggesting that the exchange between HM^{2+} and $CTMA^+$ cations was not complete. The sample was thus subjected to additional exchanges, and the structure modifications were monitored by X-ray diffraction, IR, and ^{29}Si NMR spectroscopies. After four exchanges, both the X-ray diffraction pattern and the ^{29}Si MAS NMR spectrum remained unchanged, suggesting a complete exchange, which was confirmed by ^{13}C NMR.

Figure 10. ^{29}Si MAS NMR spectra of HM-silicate (a) and CTMA/HM-silicate after one (a) and four (b) exchanges with an aqueous solution of CTMABr.

Figure 11. X-ray diffraction patterns of HM-silicate (a), NH$_4$/HM-silicate (b), and CTMA/HM-silicate (c).

The X-ray powder diffraction pattern of the corresponding material is still consistent with a lamellar structure characterized by a *d* spacing of 27.2 Å (Figure 9). A very similar value for the XRD *d* spacing has been reported by Huo et al.[23] for a series of lamellar metal oxides or phosphates prepared in the presence of surfactants with alkyl chains in C$_{16}$. For several materials, the *d* spacing was comprised between 25.8 and 28.3 Å. As previously, the infrared spectrum was not modified and was similar to that of HM-silicate before treatment. The ^{29}Si MAS NMR spectrum of CTMA/HM-silicate obtained after four exchanges is composed of four lines at ca. −94.9, −99.8, −105.8, and −110.9 ppm with intensity ratios 1:2:1:1 (Figure 10). ^{1}H−^{29}Si CP/MAS experiments performed at low spinning speeds revealed that the resonance at −99.8 ppm is actually the superposition of two signals with the same intensity assigned to Q^4 and Q^3 species.
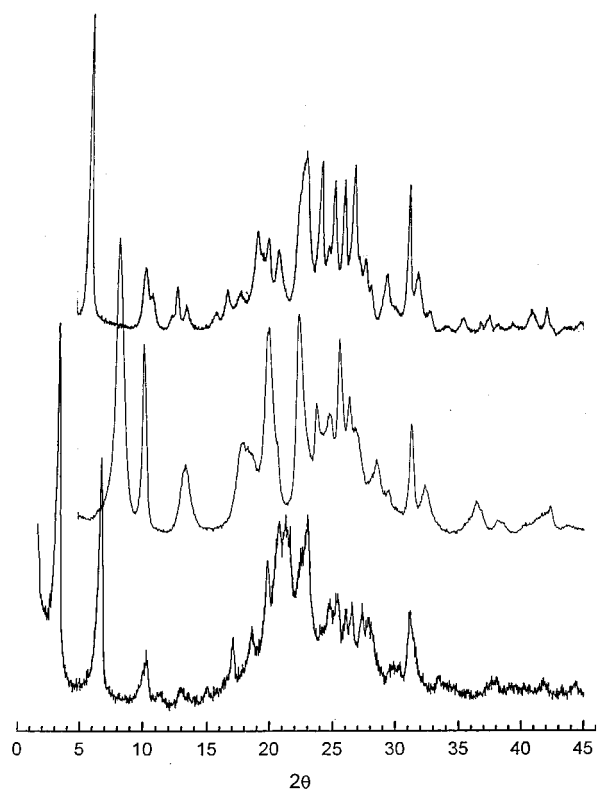
The evolution of ^{29}Si NMR spectra with the number of chemical exchanges shows that the technique is very sensitive to the nature of organic species between the silica layers. By their specific interactions with silica species as well as their arrangement in the interlayer space, these molecules probably modify the local environment around silicon atoms in terms of Si−O−Si bond lengths and angles.

HM-silicate also displays intercalation properties toward small molecules. The X-ray diffraction pattern of NH$_4$/HM-silicate obtained by reacting HM-silicate with an aqueous solution of NH$_4$Cl shows that the basal reflection has shifted toward high θ values, an indication of a compression of the interlayer distance (Figure 11). The corresponding *d* spacing is 10.13 Å. Taking the value of 2.9 Å for the mean diameter of NH$_4^+$ cations leads to a thickness for silica layers of approximately 7.2 Å, in excellent agreement with previous determinations. Most of the X-ray reflections are well-defined, thus supporting the crystalline nature of NH$_4$/HM-silicate. By comparing the X-ray patterns in Figure 11, it is clear that some of the diffraction peaks are not affected by the intercalation process. This is particularly the case for peaks at $2\theta = 10.3°$ and $31.2°$. Note that the same peaks were observed in the X-ray pattern of the TEA-layered material (Figure 1), which suggests once more that the two layered compounds could possess silica layers with very similar structures. As previously, intercalation of ammonium ions did not significantly modify the framework infrared spectrum of the material. The ^{29}Si MAS NMR spectrum of NH$_4$/HM-silicate still shows five resonances with equal intensities at ca. −97.5, −99.8, −103.4, −106.9, and −112.6 ppm.

The TEA-layered material displays similar intercalation properties toward long alkylammonium cations such as CTMA$^+$ or small cations such as tetramethylammonium (TMA$^+$) cations. As for the previous solid, the nature of the organic molecule modifies the distance between silica layers without degradation of the crystallinity. The *d*-spacing value corresponding to the basal X-ray diffraction reflection of the TMA/TEA material is 6.4 Å, very close to that observed for HM-silicate. Moreover, the small differences that were observed

(20) Roth, W. J.; Kresge, C. T.; Vartuli, J. C.; Leonowicz, M. E.; Fung, A. S.; McCullen, S. B. *Catalysis by Microporous Materials*; Beyer, H. K., Karge, H. G., Kiricsi, I., B.Nagy, J., Eds.; *Stud. Surf. Sci. Catal.* **1995**, *94*, 301.

(21) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2317.

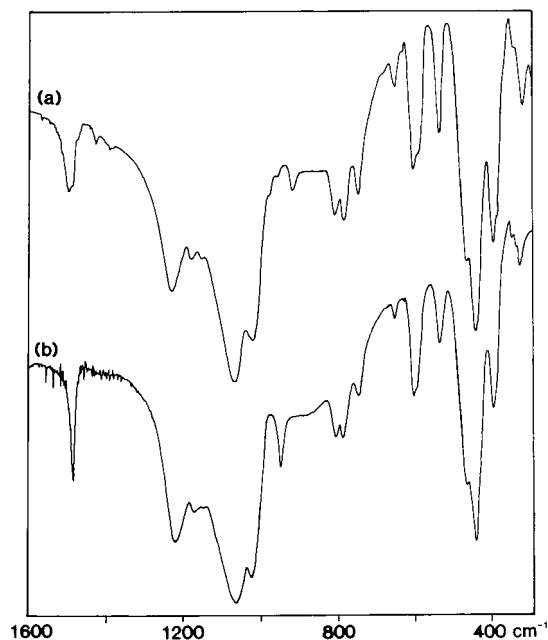(22) Yanagisawa, T.; Shimizu, T.; Kiroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.

(23) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.

**Figure 12.** Framework infrared spectra of HM-silicate (a) and the TMA/TEA-layered material (b).

between HM and TEA-layered materials in the region of the infrared spectrum around 800 cm^{-1} (Figure 5) are no longer observed after intercalation. The infrared spectrum of the TMA/TEA-layered compound is strictly the same as that of HM-silicate (Figure 12), which confirms that the two solids are probably similar materials. The similarity is also supported by ^{29}Si NMR: the spectrum of the TMA/TEA-layered compound shows five resonances whose chemical shifts are very close to those observed for HM-silicate.

Crystallization of ZSM-48 and Beta Zeolites. We have shown that HM and TEA-layered materials were obtained prior to the crystallization of zeolites ZSM-48 and beta, respectively. Actually, highly crystalline solids can only be obtained within a relatively short synthesis period. Experiments performed by recovering the solid phase at different time intervals indicated that these compounds are not stable at relatively high temperature under hydrothermal conditions. These observations tend to show that the final zeolite, obtained for long crystallization periods, is probably not formed via a direct transformation of a two-dimensional layered structure. In the case where layered compounds are effectively zeolite precursors, one can expect some similarities or relations between the structures of the two materials. As an example, the X-ray diffraction pattern of PREFER possesses reflections similar to those of the zeolite, suggesting that ferrierite sheets are already present in the layered compound.[24] In the present case, neither HM-silicate nor the TEA-layered material showed X-ray diffraction peaks that could be assigned to ZSM-48 or beta zeolites, respectively. Moreover, materials such as PREFER or ERB-1 do not lead to zeolitic frameworks under hydrothermal conditions. The building up of the three-dimensional network necessitates the calcination of the precursor at high temperature and the condensation of silanol groups to connect two-dimensional layers
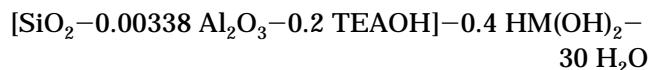
(24) Schreyer, L.; Caullet, P.; Mougenel, J. C.; Guth, J. L.; Marler, B. *J. Chem. Soc., Chem. Commun.* **1995**, 2187.

together.[5,24] A completely different behavior is observed for HM and TEA-layered compounds; their structure collapses upon removal of the organics, and the amorphous solid does not recrystallize at higher temperatures, as is the case for PREFER.

A detailed characterization of the materials has shown that the structures of HM and TEA-layered compounds are probably very similar. It seems therefore difficult to imagine that they can lead to either ZSM-48 or beta zeolites, whose structures have nothing in common. Another argument against the formation of the zeolites via intermediate layered structures can be obtained by chemical analysis of the materials. As already reported, chemical analysis of the TEA-aluminosilicate gave Si/Al = 148, while this ratio decreases to 57 in the beta zeolite obtained from the same gel composition after 15 days of crystallization. This difference can only be explained assuming a partial (or even complete) dissolution of the layered compound in the synthesis medium. Under such conditions, zeolites would be obtained from silicate or aluminosilicate species in solution, resulting from the dissolution of an amorphous compound formed upon degradation of the layered precursors at high temperature.

To check the validity of this assumption, additional syntheses have been performed starting from HM or TEA-layered materials as silicon and aluminum sources. Layered materials were first dispersed in water, and the corresponding mixtures were heated under stirring at 180 and 135 °C for the HM and TEA compounds, respectively. In both cases, only amorphous solids, free from organic molecules, were obtained after 5 days. These preliminary experiments clearly show that the zeolites cannot crystallize in the absence of organic molecules in the reaction medium, thus refuting the possibility of a solid-state rearrangement of the two-dimensional structures to zeolites at high temperature. Furthermore, a sample of HM-layered compound prepared in the presence of aluminum (Si/Al = 182 in the solid) was dispersed in an aqueous solution of TEAOH, and the resulting mixture with the following composition

$$[SiO_2 - 0.00275\ Al_2O_3 - 0.1\ HM^{2+}] - 0.53\ TEAOH - 6.8\ H_2O$$
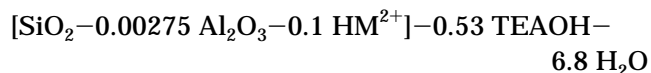
was heated at 135 °C under stirring (60 rpm) for 15 days. After this period, a solid phase was recovered whose X-ray diffraction pattern was characteristic of a beta zeolite. Chemical analysis of the solid showed that the zeolite contained more aluminum than the starting layered precursor, indicating that the latter had been dissolved and that a significant proportion of silica species remained in solution. A second experiment was performed by dispersing the TEA-layered material in an aqueous solution of hexamethonium hydroxide, HM-(OH)$_2$. The mixture, with the composition

$$[SiO_2 - 0.00338\ Al_2O_3 - 0.2\ TEAOH] - 0.4\ HM(OH)_2 - 30\ H_2O$$

was heated at 180 °C under stirring for 6 days. The X-ray diffraction pattern of the obtained product showed that ZSM-48 had been formed.

Finally, both the HM and TEA-layered materials have been dispersed in aqueous solutions of tetrapropylammonium hydroxide (TPAOH) to obtain gels with Si/TPAOH = 0.4 and H_2O/SiO_2 = 40. Whatever the nature of the precursor, ZSM-5 (or silicalite-1) was formed after hydrothermal treatment at 175 °C for 10 days.

These experiments clearly show that the structure of the zeolite and that of the layered compound are not related. If the TEA-layered material was really a precursor of zeolite beta, one would expect the crystallization of this zeolite in all media. Actually, the structure of the zeolite seems to be directed by the nature of the organic molecule in solution. It is thus not surprising that beta zeolite crystallizes after the formation of the TEA-layered material since TEA^+ species, which direct the crystallization of the zeolite, are the only organic cations in solution. However, changing the TEA^+ species in solution for HM^{2+} or TPA^+ cations leads to the crystallization of zeolites with different structures. These observations indicate that the role of the layered material is to provide the reaction medium with silicon and aluminum species and that the structure of the zeolite depends only on the nature of the ammonium ions present in the liquid phase.

Conclusion

Layered crystalline materials have been observed and isolated during the crystallization of ZSM-48 and beta zeolites with hexamethonium and tetraethylammonium cations, respectively. These structures are formed at short crystallization times but are not stable under hydrothermal conditions. Their structure collapses with synthesis time until a completely amorphous compound is formed. The crystallization of the final zeolite starts only after the degradation of the layered material, and the two structures do not coexist during the crystallization process. The stability of these layered compounds can be increased by carrying out syntheses at lower temperatures. HM and TEA-layered materials obtained from different gel compositions possess the same infrared spectrum, suggesting that the structures of inorganic layers are probably very similar. The similarity is supported by the presence of five nonequivalent silicon species with the same intensity in the ^{29}Si NMR spectra of both materials. These layered structures display intercalation properties toward quaternary ammonium cations. The basal reflection of the X-ray diffraction pattern shows that the interlayer distance can be increased or decreased, depending on the size of the intercalated molecule, but without modification of the crystallinity.

The evolution of these materials in the course of crystallization as well as the lack of relationship between their structure and that of the corresponding zeolite obtained for longer crystallization periods suggests that they are not zeolite precursors, as was previously claimed for zeolite beta. The present data clearly show that layered materials are dissolved in the reaction medium, thus providing silicate and aluminosilicate species necessary for the crystallization of the zeolite. The crystallization of zeolites with various structures when layered compounds are in the presence of different templating molecules strongly supports this synthesis mechanism.