Identification of a Double Five-ring Silicate, a Possible Precursor in the Synthesis of ZSM-5

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A double five-ring silicate has been identified for the first time in the ZSM-5 synthesis mixture using ^{29}Si n.m.r., attenuated total reflection Fourier transform-infrared spectroscopy, and mass spectrometry; a redistribution of the silicate species present in the solution phase has been observed after the addition of organic solvents to the ZSM-5 synthesis mixture.

ZSM-5 is most effectively prepared from slurries containing silica, alumina, sodium hydroxide, and tetrapropylammonium hydroxide (TPAH), yielding ZSM-5 of a high crystallographic purity. The role of the organic base in the synthesis of the zeolite is still hardly understood, although generally a clathrating–templating role has been accepted.[1–4] For this reason we have recently studied the nature of the organic base occluded in the ZSM-5 framework, using solid-state ^{13}C n.m.r. spectroscopy.[5,6]

Here we report some preliminary results of the ordering in solution of silicates in the presence of TPAH in the synthesis of ZSM-5. The silicates formed were characterized by ^{29}Si n.m.r., attenuated total reflection Fourier transform-infrared (a.t.r. F.t.-i.r.) spectroscopy, and mass spectrometry. ^{29}Si

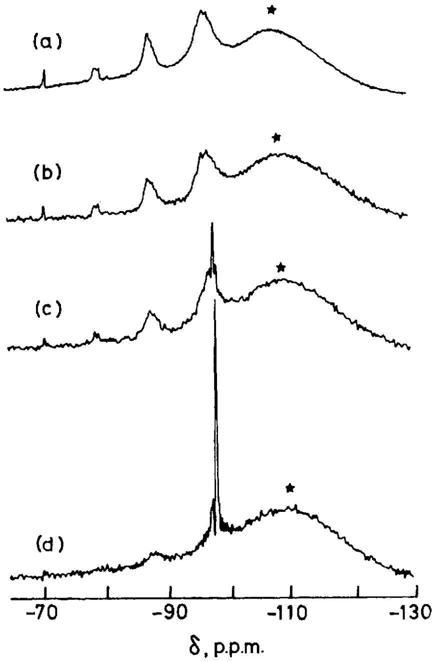

Figure 1. ^{29}Si N.m.r. spectra of: (a) ZSM-5 synthesis mixture with composition 288 SiO_2, Al_2O_3, 9 Na_2O, 42 TPA_2O, 5400 H_2O; ZSM-5 mixture of (a) after addition of DMSO; (b), 9/1; v/v; (c), 3/1; v/v; (d), 1/1; v/v. The resonance marked with an asterisk (*) is from the glass n.m.r. tube.

N.m.r. has been used previously in the identification of silicates, especially of double, three-, four-, and five-ring silicates in tetramethyl-, tetraethyl-, tetrapropyl-, and tetra-butyl-ammonium hydroxide–silica solutions.[7–17] So far, TPAH–SiO_2 solutions have not contained a large amount of such a unique silicate.[16,17]

Figure 1(a) shows the ^{29}Si n.m.r. spectrum of a ZSM-5 synthesis slurry having the overall composition: 288 SiO_2, Al_2O_3, 9 Na_2O, 42 TPA_2O, 5400 H_2O. The ^{29}Si n.m.r. spectrum indicates that many silicates are present in the synthesis mixture, from monomers to highly branched silicates. The identification of a unique silicate, which might be a precursor in the ZSM-5 synthesis, seems highly unlikely in such a synthesis mixture. However, the addition of organic solvents such as methanol, ethanol, or dimethyl sulphoxide (DMSO) drastically reorganizes the silicate structures present in solution and in their presence one sharp ^{29}Si n.m.r. signal was found at −98 p.p.m. Figure 1 shows that upon increasing the amount of organic additive (DMSO) the intensity of the −98 p.p.m. signal increases; at the same time the concentration of all other silicates is reduced.

The observation of only one ^{29}Si n.m.r. signal indicates that a highly symmetrical species has been formed. In contrast, the addition of acetone and tetrahydrofuran only reduced the intensities of the signals, whereas following addition of 1,4-dioxane or dimethylformamide no ^{29}Si n.m.r. spectra could be obtained, as a result of too strong a gel formation. The chemical shift (−98 p.p.m.) of the species formed after the addition of the organic solvents suggests that a double four-, five-, or six-ring silicate has been formed. Since the shifts of these silicates differ by only 1 p.p.m.,[10,13] n.m.r. cannot differentiate between these structures.

The nature of the silicate was identified further using a.t.r. Ft.-i.r. spectroscopy. Normally, i.r. spectroscopy is unsuitable for studying water solutions because the water absorptions are too strong. With a.t.r., however, unlike conventional transmission spectroscopy, the i.r. radiation only partially penetrates the sample (up to a few micrometres), thereby reducing the water absorptions. Figure 2 demonstrates the possibilities of this technique in combination with Fourier transformation in the study of silica, in aqueous solutions. Spectrum 2(a) shows the absorption bands of a normal ZSM-5 synthesis mixture (*cf.* Figure 1) in the region between 2000 and 600 cm^{-1}, after compensating for the i.r. absorptions of TPAH and H_2O. The addition of DMSO results in a better defined spectrum [see Figure 2(b)], this indicating the formation of a silicate having absorption bands at 1126,† 1011,† and 949 cm^{-1} (spectrum obtained after compensating for TPAH, H_2O, and DMSO). Most probably the 949 cm^{-1} band is due to a distortion of a DMSO vibration, since in the corresponding MeOH and EtOH solutions, only a weak shoulder is observed at this frequency. The a.t.r. Ft.-i.r. measurements eliminate the possibility of the formation of a double four-ring silicate, since for this silicate, separately, absorption bands at 1081 and 1026 cm^{-1} were obtained[18] (with a possible shoulder at 850 cm^{-1}) in a tetramethylammonium hydroxide–SiO_2 solution.‡

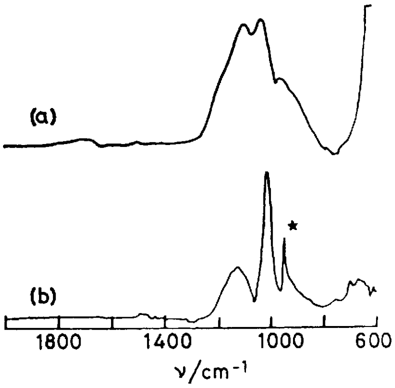

Figure 2. Attenuated total reflection Fourier transform-infrared spectra of: (a) ZSM-5 synthesis mixture after subtraction of TPAH and H_2O; (b) ZSM-5 synthesis mixture after addition of DMSO with subtraction of TPAH, H_2O, and DMSO. The vibration marked with an asterisk (*) is due to DMSO.

Mass spectroscopy measurements on the silylated ZSM-5–organic additive mixtures together with gas chromatography (silylating agents, trade name 'Trisil,' *i.e.* hexamethyldisilazane and trimethylsilyl chloride in pyridine, obtained from Pierce Chemical Co.) in combination with the above results, revealed evidence of the formation of a double five-ring silicate after the addition of MeOH, EtOH, or DMSO. (The double five-membered ring with m/z = 1395 was the major species present in the synthesis mixture after silylation, but also a considerable amount of double four-ring silicates and a small amount of double six-ring silicates could be detected. These double four- and six-ring silicates are probably formed during the silylation procedure since ^{29}Si n.m.r. of the original ZSM-5–organic additive mixture showed only one resonance at −98 p.p.m. and a.t.r. F.t.-i.r. did not reveal evidence of the formation of a double four-ring silicate.) The double five-ring structure is easily recognized in the ZSM-5 building unit (Figure 3, ref. 19). Treatment of such a mixture in an autoclave at temperatures between 120

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† The positions of the silicate bands are slightly dependent upon the additive used.

‡ ^{29}Si N.m.r. of the same $Me_4NOH–SiO_2$ solution showed one signal at −97 p.p.m. in agreement with refs. 7 and 13.

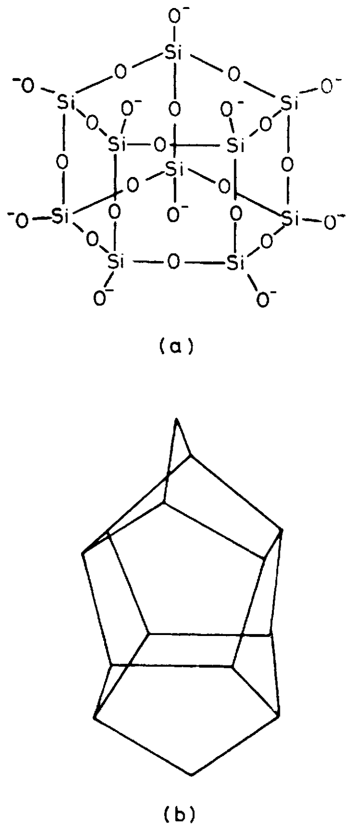

Figure 3. (a) Double five-ring silicate; (b) ZSM-5 building unit.

and 150 °C resulted in the formation, after calcination and ion exchange, of the acid (H) form of ZSM-5 of high crystallographic purity, as could be deduced from its well resolved solid-state ^{29}Si n.m.r. spectrum, which shows up to eight resonances between -110 and -118 p.p.m.[20,21] Similar results have been obtained using acetone and 1,4-dioxane. The addition of organic solvents has been claimed to be effective for the synthesis of microcrystalline faujasite.[22] Furthermore, silylation of the original ZSM-5 synthesis mixture indicated that a double five-ring structure is also present in this slurry, although in a much lower quantity.

We conclude that in the ZSM-5 synthesis mixture different silicates (for convenience given in the unprotonated form) are in equilibrium (1). The presence of the double five-ring silicate, which has now been identified both in pure ZSM-5 synthesis mixtures and (in a high quantity) in ZSM-5–organic mixtures, probably plays a key role in this zeolite synthesis. (It is of note that ^{29}Si n.m.r. only detects the soluble silicates and yields no information about the solid silicates that might also direct the ZSM-5 formation.) ZSM-5 may only be formed from the double five-ring intermediate, while the other silicates are expected to yield amorphous material and/or other zeolite structures. During the formation of ZSM-5 from the double five-ring silicate, new rings are formed under the influence of tetrapropylammonium ions. The supply of SiO_4^{4-} ions from silicic acid ($SiO_2{\cdot}xH_2O$) is provided by the OH^- ions. When the silicic acid is depolymerized, the concentration of the soluble silicates decreases rapidly because of the formation of crystalline ZSM-5. This conclusion is supported by an experiment in which the concentration of the double five-ring silicate (in a ZSM-5–organic additive mixture) was followed over a period during an autoclave experiment; after 6 h at 130 °C the intensity of the double five-ring silicate n.m.r. signal was reduced to 30% of its original value and after 16 h no double five-ring signal was detected, while ZSM-5 was formed.

$$\begin{array}{l}
SiO_4^{4-} \rightleftharpoons Si_2O_7^{6-} \rightleftharpoons Si_3O_8^{8-} \rightleftharpoons Si_3O_9^{6-} \rightleftharpoons \\
\cdots Si_{10}O_{25}^{10-} \rightleftharpoons \cdots SiO_x^{y-} \\
\quad \Big\downarrow \text{ hydrothermal treatment} \\
\text{ZSM-5}
\end{array} \qquad (1)$$

We further conclude that the organic additives such as MeOH, EtOH, and DMSO favour the formation of a double five-ring silicate from the ZSM-5 synthesis mixture. Similar rapid transformations into double ring silicates have been obtained for other tetra-alkylammonium solutions[23] (alkyl = Me, Et, and Bu).

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