Synthesis of Zeolite MCM-22 Using *N*,*N*,*N*,*N*′,*N*′,*N*′-Hexamethyl-1,5-pentanediaminium and Alkali Metal Cations as Structure-directing Agents

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A novel synthesis route to the high-silica zeolite MCM-22, which includes the combined use of a flexible, linear diquaternary ion *N*,*N*,*N*,*N*′,*N*′,*N*′-hexamethyl-1,5-pentanediaminium and Na^+ or K^+, is described. Unlike the previously known organic structure-directing agents leading to the crystallization of MCM-22 and related materials, the organic additive used here was found to locate inside both the 12-ring supercages and the sinusoidal 10-ring channels of MWW topology.

MCM-22 is one of the most complex and fascinating zeolite structures discovered thus far. This high-silica zeolite is known to first crystallize as a lamellar precursor that undergoes dehydroxylation upon calcination between the layered sheets, to generate the so-called MWW structure consisting of two independent 10-ring channels; one formed by two-dimensional sinusoidal channels, and the other by large supercages with 7.1 Å in diameter and 18.2 Å in height that can be accessible through 10-ring widows only.[1] Thus, it is not difficult to expect that MCM-22 would be potentially useful as a shape selective catalyst for many hydrocarbon conversions, especially for those involving bulky transition state intermediates.

MCM-22 has three precedents denoted as PSH-3, SSZ-25, and ERB-1 in the literature.[2] While the synthesis of PSH-3 and MCM-22 includes the use of hexamethyleneimine as an organic structure-directing agent (SDA) together with Na^+, SSZ-25 has crystallized in the presence of a specialized organic cation, *N*,*N*,*N*-trimethyl-1-adamantylammonium, and K^+. On the other hand, the borosilicate ERB-1 can be synthesized using piperidine, both with and without alkali metal cations present. In addition to these organic SDAs, there are a number of other organic molecules capable of crystallizing MWW-type zeolites when used in conjunction with a small amine like isobutylamine.[3] To our knowledge, however, all the synthesis routes to MCM-22 and related materials published to date share in common the use of cyclic or polycyclic organic additives. Here we show that the *N*,*N*,*N*,*N*′,*N*′,*N*′-hexamethyl-1,5-pentanediaminium (Me_6-diquat-5) ion, whose shape and size are notably different from those of any of known organic SDAs yielding MWW-type microporous materials, can also produce the same zeolite structure, when the concentrations of Al and alkali metal cations in the gel are properly selected. This flexible, noncyclic diquaternary cation has previously been shown to direct the formation of EU-1 and ZSM-48 zeolites.[4]

In a typical synthesis of MCM-22, 0.32 g of $Al(NO_3)_3 \cdot 9H_2O$ (98%, Junsei) and 1.47 g of NaOH (50% aqueous solution, Aldrich) were dissolved into 14.69 g of H_2O. To this clear solution, 3.75 g of colloidal silica (Ludox AS-40, Dupont) and 1.33 g of Me_6-diquat-5 dibromide were added. The Me_6-diquat-5 dibromide used here was prepared by refluxing 1,5-dibromopentane (97%, Aldrich) with an excess of trimethylamine (33 wt% solution in ethanol, Acros) in ethanol as a solvent overnight. The oxide composition of the synthesis mixture was $4.5Me_6\text{-diquat-}5 \cdot 11.0Na_2O \cdot 0.5Al_2O_3 \cdot 30SiO_2 \cdot 1200H_2O$. After stirring at room temperature for 1 day, the final gel was transferred to Teflon-lined 45-mL autoclaves and heated at 160°C under rotation (100 rpm) for 7 days. The resulting mixture was then filtered and washed with deionized water. About 5.0 g of solid per 100 g of the initial gel were obtained (taking into account a 22.1% weight loss upon calcination at 800°C, this amounts to ca. 50% incorporation of the silica and alumina employed). The typical powder XRD patterns of the as-made and proton forms of MCM-22 prepared here are given in Figure 1. The pattern of as-made MCM-22 is in good agreement with that of the layered precursor of MWW topology.[3,5] Also, the changes in the XRD pattern of MCM-22 induced by calcination at 550°C were found to be consistent with those already described for this type of materials.[5] From N_2 adsorption experiments on H-MCM-22, a BET surface area of $438\,m^2\,g^{-1}$ was derived. SEM photographs show that our MCM-22 appears as agglomerates of thin sheets with ca. 0.5 µm in length and 0.05 µm in thickness, which is quite similar to the morphology previously reported.[6] Elemental analysis reveals that the SiO_2/Al_2O_3 ratio (38) in as-made MCM-22 is fairly lower than that (60) in the initial gel, while the organic content is *ca.* 17 wt% (C, 11.78; H, 2.87; N, 2.55) with a C/N ratio of 5.4 that is close to the value of Me_6-diquat-5 (5.5).

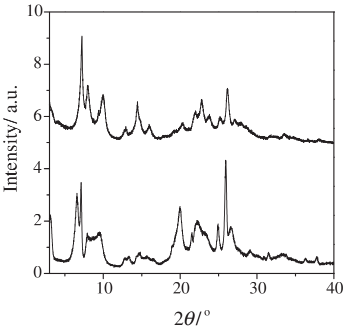

Figure 1. Powder XRD patterns of the (a) as-made and (b) proton forms of MCM-22. Rigaku 2500H diffractometer, Cu K_α radiation, 0.01° 2θ step size and 1 s count time.

Figure 2 compares the ^1H-^{13}C CP MAS NMR spectrum of as-made MCM-22 with the liquid ^{13}C NMR spectrum of the Me_6-diquat-5 dibromide salt. Notice that the resonance of the methyl carbons of the organic species in as-made MCM-22

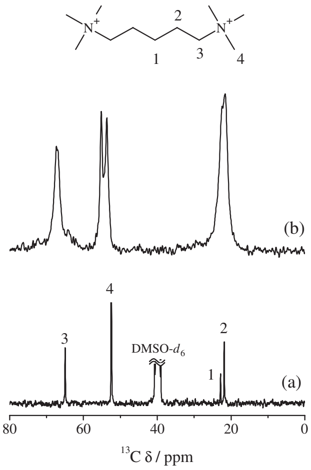

Figure 2. ^{13}C NMR spectra of organic SDA, Me_6-diquat-5: (a) ^{13}C NMR of Me_6-diquat-5 dibromide in DMSO-d_6 solution and (b) ^{1}H-^{13}C CP MAS NMR of as-made MCM-22 with Me_6-diquat-5 occluded in the pores, which was recorded on a Bruker DSX 300 at 5.0 kHz spinning rate, 1 s recycle delay, 75.467 MHz, π/2 rad, 5 μs pulse length, 1 ms contact time, and 4000 scans.

splits into two peaks at 55.2 and 53.7 ppm, unlike that of the corresponding carbons of free Me_6-diquat-5. The same trend can also be observed for the case of the methylene carbons bonded to the nitrogen of the occluded Me_6-diquat-5 molecules. On the other hand, the dimethylformamide treatment (1 g solid/ 50 mL solvent) of as-made MCM-22 at 160°C for 2 days in the Teflon-lined autoclave gave no noticeable changes in the number and position of ^{13}C NMR resonances. However, the organics liberated by dissolution of as-made MCM-22 in HF were found to exhibit the liquid ^{13}C NMR spectrum essentially identical to that of free Me_6-diquat-5. Therefore, it is clear that two different degrees of geometric constraints and van der Waals interactions with the zeolite framework are imposed on the methyl groups of Me_6-diquat-5 inside the MCM-22 pores. As described above, the MWW structure contains the sinusoidal 10-ring channels as well as the supercages that are large enough to host Me_6-diquat-5. The fact that the pore dimension (4.1 × 5.1 Å) of sinusoidal channels in MCM-22 is slightly larger than the girth (3.9 Å) of the trimethylammonium groups of Me_6-diquat-5[7] led us to conclude that the flexible Me_6-diquat-5 cations are located not only inside the 12-ring supercages but also inside the sinusoidal 10-ring channels, which is substantially different than the case of already known organic SDAs that cannot stabilize the sinusoidal channels of the structural model proposed for MCM-22 due to their large sizes.

While the synthesis procedure described above proved to be highly reproducible, the overall synthetic results of this study reveal that the oxide composition range yielding pure MCM-22 in the presence of Me_6-diquat-5 is rather narrow. When using a sodium aluminosilicate gel with $SiO_2/Al_2O_3 = 60$ and $NaOH/SiO_2 = 0.60$, for example, we always obtained MCM-22 after heating at 160°C for 7 days. This is even true in the case of replacing NaOH by the equivalent amount of KOH under the identical conditions. When the synthesis conditions were selected so that $NaOH/SiO_2 < 0.60$ or > 0.73, however, we were able to crystallize the other three zeolitic phases (i.e., mordenite, ZSM-12, and EU-1) in their pure form. Also, ZSM-48 was the product obtained from a gel with $SiO_2/Al_2O_3 = \infty$ and $NaOH/SiO_2 = 0.33$. Like MCM-22, these four zeolites were shown by TGA/DTA to contain significant amounts (>12 wt%) of organic species. This suggests that the structure-directing ability of Me_6-diquat-5 itself is not strong enough to govern the synthesis of any of zeolites prepared here. Due to notable difference in geometrical restrictions imposed by their pore structures, however, the Me_6-diquat-5 ended up occluded within the crystallized products should adopt conformations that are distinctly different from one another and are actually relevant ones acting as phase selectivity factors through stabilizing nuclei for particular zeolite structures, respectively. Apparently, the type of the conformations of such a flexible molecule dominant at zeolite synthesis conditions can differ significantly according to the nature and extent of interactions between the organic SDA and the surrounding inorganic species in synthesis mixtures. The success of MCM-22 synthesis in the presence of a linear Me_6-diquat-5 ion, the shape and size of which are quite different from those of any of the existing organic SDAs leading to the formation of MWW-type zeolites, strongly supports our recent proposal that the modification of conformations of flexible organic SDAs such as linear diquaternary alkylammonium ions with aliphatic and/or cyclic moieties by varying the concentrations of Al and/or alkali cations in zeolite synthesis mixtures may be an area of considerable possibility for finding new materials.[8] Zeolite syntheses using a series of Me_6-diquat-n ions with $n = 3$–10 from synthesis mixtures with wide ranges of SiO_2/Al_2O_3 and MOH/SiO_2 ratios (M = Na or K), together with extensive investigations of the host–guest interactions in zeolites prepared with Me_6-diquat-5, are currently underway in our laboratory.

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