Synthesis of zeolites P1 and SUZ-4 through a synergy of organic *N,N,N,N′,N′,N′*-hexaethylpentanediammonium and inorganic cations†

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Zeolites P1 and SUZ-4 with enhanced Si/Al ratios (*ca.* 4.9 and 8.2) compared to previously reported isostructural materials have been synthesized in the presence of *N,N,N,N′,N′,N′*-hexaethylpentanediammonium together with Na+ and K+ ions, respectively.

The use of the doubly charged cation *N,N,N,N′,N′,N′*-hexaethylpentanediammonium (Et_6-diquat-5) as an organic structure-directing agent (SDA) in the synthesis of zeolites was first attempted by Valyocsik and Page in 1986.[1] It has been shown that this diquarternary cation can direct the crystallization of ZSM-57 (MFS topology) with the intersecting 10- and 8-ring channel system when used together with Na^+ ions.[2] Very recently, we have studied zeolite synthesis related to the use of a series of diquarternary cations with different chain lengths and found that the type and amount of alkali metal cations added to the synthesis mixture may play a major role in determining the phase selectivity of the crystallization.[3]

Zeolite P1 is the synthetic analogue of the GIS-type zeolites and contains a two-dimensional pore system with two intersecting 8-ring channels.[4] On the other hand, SUZ-4,[5,6] a new zeolite closely related to ferrierite and ZSM-57, has been considered to have a topology that corresponds to the hypothetical model 5b described by Gramlich-Meier.[7] To our knowledge, the only organic SDA leading to the successful SUZ-4 formation is the tetraethylammonium cation.[8] Here, we report for the first time, the synthesis of zeolites P1 and SUZ-4 from sodium- and potassium-containing aluminosilicate gels in the presence of Et_6-diquat-5, a new organic SDA for these structure-types of materials.

In a typical synthesis of zeolite P1, 0.48 g of $Al(NO_3)_3{\cdot}9H_2O$ (98%, Junsei) and 2.20 g of NaOH (50% aqueous solution, Aldrich) were dissolved into 22.01 g of H_2O. To this clear solution, 5.63 g of colloidal silica (Ludox AS-40, DuPont) and 2.48 g of Et_6-diquat-5 dibromide prepared according to the procedure described elsewhere[1] were added. The oxide composition of the resulting gel was $4.5Et_6$-diquat-5 : $11.0Na_2O : 1.0Al_2O_3 : 30SiO_2 : 1200H_2O$. For the crystallization of SUZ-4, NaOH was replaced by an equivalent amount of KOH (45% aqueous solution, Aldrich) under the conditions described above. After stirring at room temperature for 1 day, the final synthesis mixture was transferred to Teflon-lined 45 mL autoclaves and heated at 160 °C under slow rotation (60 rpm) for 8 days. The white solid products were recovered by filtration, washed repeatedly water, and then dried overnight at room temperature.

Fig. 1 shows the typical powder X-ray diffraction patterns (Rigaku Miniflex, Cu-Ka radiation) of P1 and SUZ-4 prepared here. Comparison of the patterns in Fig. 1 with those in the literature[6,9] reveals that both materials are highly crystalline and no reflections other than those from the corresponding zeolites are observed. This can be further supported by the N_2 adsorption data (Micromeritics ASAP 2410) of P1 and SUZ-4 calcined at 500 °C for 6 h to remove the occluded organic species, from which the BET surface areas of 124 and 370 $m^2\ g^{-1}$ were derived, respectively. SEM photographs (JEOL JSM-6300) show that zeolite P1 appears as agglomerates of small (1.5–2.0 μm), heavily overlapped cuboids, while SUZ-4 consists of needle-like crystals that are *ca.* 1 μm in length and 0.2 μm in diameter. On the other hand, it can be seen from the ^{13}C-^1H CP/MAS NMR spectra (Fig. SI 1, ESI†) of as-synthesized P1 and SUZ-4 that both samples exhibit three main resonances around δ 54, 21 and 8, which can be assigned to the methylene carbons bonded to the nitrogen, the methylene carbons in the pentyl chain and the methyl carbons in the ethyl groups of Et_6-diquat-5, respectively. This indicates that the organic SDA remains intact upon its occlusion in the P1 and SUZ-4 pores. A combination of elemental and thermal analyses reveals, within experimental error, that as-synthesized P1 and SUZ-4 zeolites have the chemical compositions $(Et_6\text{-diquat-5})_{0.6}Na_{1.8}Al_{2.7}Si_{13.3}O_{32}{\cdot}2.0H_2O$ and $(Et_6\text{-diquat-5})_{1.2}K_{2.0}Al_{3.9}Si_{32.1}O_{72}{\cdot}4.8H_2O$, respectively. Thus, there is a small but non-negligible dissimilarity between the amount of Al and the sum of Et_6-diquat-5 and alkali metal cations for the unit cell formula of each material. This suggests that a portion of the organic occluded is present in either bromide or hydroxide form to act as a space-filling species. Also, it should be noted that the Si/Al ratios (4.9 and 8.2) of P1 and SUZ-4 zeolites prepared here are higher than those of previously known isostructural materials. The Si/Al ratios for all the natural and synthetic GIS-type zeolites reported so far are always in the range 1.0–3.2,[4,10] while SUZ-4 materials are known to have a narrow Si/Al ratio range of 6.2–7.1.[5,6,8] The enhanced Si/Al ratios of our P1 and SUZ-4 zeolites can be rationalized by considering that the length (*ca.* 15 Å) of the Et_6-diquat-5 used as an organic SDA here is much larger than that of the already known SDAs (*e.g.* tetramethylammonium and tetraethylammonium cations) for these materials.

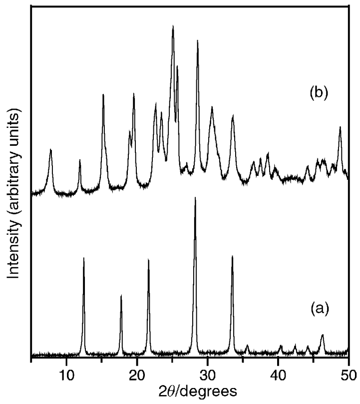

Fig. 1 Powder X-ray diffraction patterns of as-synthesized (a) P1 and (b) SUZ-4. Rigaku Miniflex diffractometer, Cu-Ka radiation, 0.02° 2θ step size and 0.50 s count time.

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† Electronic supplementary information (ESI) available: Fig. SI 1 and 2 (^{13}C–^1H CP/MAS and ^{27}Al NMR Spectra for P1 and SUZ-4). See http://www.rsc.org/suppdata/cc/b0/b004004p/

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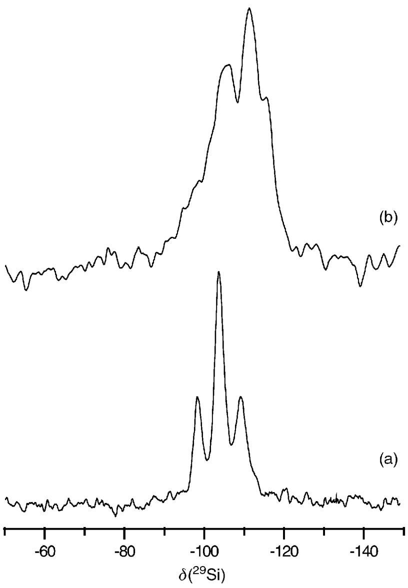

Fig. 2 ^{29}Si MAS NMR spectra of as-synthesized (a) P1 and (b) SUZ-4 zeolites. Spectra recorded on a Bruker DSX 400 at 12 kHz spinning rate, 60 s recycle delay, 79.459 MHz, $\pi/5$ rad, 2 μs pulse length, 1200 scans.

The ^{27}Al MAS NMR measurements (Bruker DSX 400, 13.0 kHz spinning rate) show that as synthesized P1 and SUZ-4 exhibit only one line at δ 58.2 and 52.7, respectively, typical of tetrahedral Al sites in zeolites (Fig. SI 2, ESI†). The ^{29}Si MAS NMR spectra of these phases are shown in Fig. 2. The spectrum of zeolite P1 is characterized by three ^{9}Si resonances at δ −109.8, −104.1 and −98.6, assigned to Si(nAl) species with n = 0, 1 and 2, respectively. Deconvolution of this spectrum allowed us to calculate a Si/Al ratio of 4.5 for our P1 that is in good agreement with the value determined from elemental analysis. On the other hand, the ^{29}Si MAS NMR spectrum of SUZ-4 shows three main resonances at −115.1, −111.3 and −106.8. We note here that the high-field resonance has not been clearly found in the reported spectrum of an SUZ-4 material with Si/Al = 6.4.[9] This again confirms the enhanced Si/Al ratio of SUZ-4 prepared here, although the existence of multiple T-sites in the proposed framework of SUZ-4 makes it impossible to determine accurately the framework Si/Al ratio from its ^{29}Si MAS NMR spectrum at this time. Further details on the physicochemical properties of our P1 and SUZ-4 will be given elsewhere.[11]

The overall synthetic results of this study reveal that the crystallization conditions and the oxide composition of synthesis mixtures yielding pure P1 or SUZ-4 in the presence of Et$_6$-diquat-5 are restricted within narrow limits, which is quite similar to the trend found in the synthesis of ZSM-57 using the same organic SDA.[3] When trying to reproduce the synthesis of zeolite P1 under static conditions, for example, the synthesis mixture remains amorphous even after heating at 160 °C for 2 weeks. By contrast, a MOR zeolite is the phase that crystallizes from the synthesis mixture with Si/Al = 20 under stirring in conditions described above. Thus, it appears that the structure-directing ability of the organic Et$_6$-diquat-5 itself is not strong enough to govern the crystallization of P1 and SUZ-4. This suggests that the synergy of alkali metal cations and a particular organic Et$_6$-diquat-5 may be a critical factor affecting the phase selectivity of the crystallization, although the exact role of alkali cations in the Et$_6$-diquat-5-mediated synthesis of P1, SUZ-4, and ZSM-57 remains to be elucidated. In order to follow a more rigorous study on this issue, extensive investigations of the host–guest interactions in these zeolites are currently underway in our laboratory.

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Notes and references

1 E. W. Valyocsik and N. M. Page, *Eur. Pat. Appl.*, 174121A2, 1986.
2 J. L. Schlenker, J. B. Higgins and E. W. Valyocsik, *Zeolites*, 1990, **10**, 293.
3 S.-H. Lee, D.-K. Lee, C.-H. Shin, W. M. Lee and S. B. Hong, *J. Catal.*, in press.
4 R. Szostak, *Handbook of Molecular Sieves*, Van Nostrand Reinhold, New York, 1992.
5 S. I. Barri, *US Pat.*, 5118483, 1992.
6 S. L. Lawton, J. M. Bennett, J. L. Schlenker and M. K. Rubin, *J. Chem. Soc., Chem. Commun.*, 1993, 894.
7 R. Gramlich-Meier, *Z. Kristallogr.*, 1986, **177**, 237.
8 M. A. Asensi, M. A. Camblor and A. Martinez, *Microporous Mesoporous Mater.*, 1999, **28**, 427.
9 M. M. J. Treacy, J. B. Higgins and R. von Ballmoos, *Collection of Simulated XRD Patterns for Zeolites*, Elsevier, London, 1996.
10 Ch. Baerlocher and W. M. Meier, *J. Helv. Chim. Acta*, 1970, **53**, 1285.
11 W. C. Paik, C.-H. Shin and S. B. Hong, manuscript in preparation.