

Synthesis of Gmelinite and ZSM-12 Zeolites with a Polymer Template

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The zeolites gmelinite and ZSM-12 are synthesized using a cationic polymer template, both cases illustrating the templating effect; magic-angle ^{13}C n.m.r. spectra provide direct evidence that the polymer is retained in the pore system of these zeolites.

Organic species have been used as 'templates' in the synthesis of aluminosilicate and aluminophosphate molecular sieves.^{1,2} The term 'template' has been applied very loosely since a specific organic species can give rise to many different structures; conversely, a specific structure can be formed from a variety of organic species. For example, $\text{AlPO}_4\text{-5}$ can be crystallized in the presence of over twenty-five different 'templates' whereas di-*n*-propylamine can be employed to grow as many as seven different aluminophosphate structures.² A true templating effect would occur with a reaction mixture if the organic agent causes a different structure to form or a molecular sieve crystallizes from a reaction mixture which otherwise would remain amorphous.³

Clear examples of the templating effect are few.¹⁻⁴ Daniels *et al.*⁵ first reported the use of cationic polymers as templates in the crystallization of zeolites. Polymers were synthesized by reacting 1,4-diazabicyclo[2.2.2]octane (DABCO) with $\text{Br}(\text{CH}_2)_n\text{Br}$ ($n = 3, 4, 5, 6, \text{ and } 10$). With 1,4-dibromobutane ($n = 4$), the resulting polymer was designated DAB-4Br and had a weight-average molecular weight of *ca.* 10,000. Two series of experiments were conducted with the polymer templates; one at 90, and the other at 180 °C. In the absence of the polymers, zeolite Y (90 °C) and analcime (180 °C) were crystallized. With the DAB-4Br polymer, two twelve membered ring structures, gmelinite (90 °C) and mordenite (180 °C), were obtained. The DABCO unit is cylindrical with a diameter of *ca.* 6.1 Å and would thus fit into the 7–8 Å diameter channels of the zeolite. Evidence for incorporation of the DAB-4 polymer into the zeolite channel system was indirect being solely based upon chemical analysis.

Increasing interest in the field of water soluble polymers prompted us to explore further the use of the DAB-4 polymer as a template for zeolite synthesis. We aim (a) to determine if in fact the DAB-4 polymer is incorporated into the gmelinite channel system as implied by Daniels *et al.*, and (b) to explore the use of polymer templates in syntheses which involve silica only.

We synthesized the DAB-4Br polymer according to the procedure outlined by Daniels *et al.*⁵ The magic-angle spinning (m.a.s.) ^{13}C n.m.r. spectrum of the solid polymer (recorded using a Bruker MSL-300 spectrometer) (Figure 1, lower trace) is the same as that recorded for DAB-4Br dissolved in water. The peak at δ 52.2 is attributed to the carbons in the DABCO unit while the other peaks at δ 64.6 and 19.7 are assigned to the carbons in the tetramethylene moiety. Gmelinite was synthesized (also according to the procedure of Daniels *et al.*, ref. 5, Table III, Run 10) and was identified as such by X-ray powder diffraction. The m.a.s. ^{13}C

n.m.r. spectrum of the DAB-4Br/gmelinite is shown in the upper trace of Figure 1. Resonances are observed at δ 64.0, 52.9, 45.4, and 19.3. The peaks at δ 64 and 19 agree well with the spectrum of the pure polymer, but notice that the signal from the carbons in the DABCO unit now appear as two peaks. We believe this is because the two carbons in the ethylene bridges of the DABCO unit are no longer equivalent when the polymer is residing in the channels of the gmelinite. These n.m.r. data are the first direct evidence that the polymer remains intact in the pores of gmelinite, confirming the speculations of Daniels *et al.*

All of the syntheses of Daniels *et al.* used polymers with bromine as the anion and aluminium in the synthesis gels.

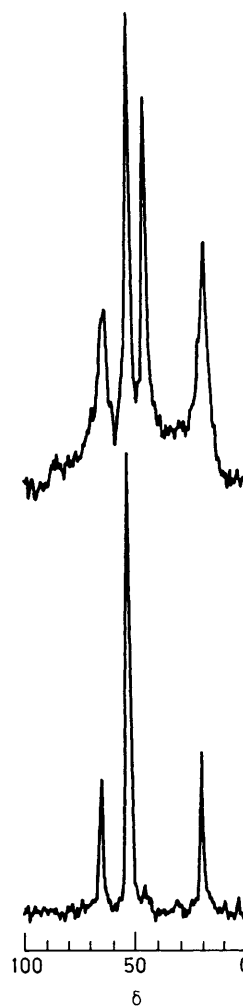
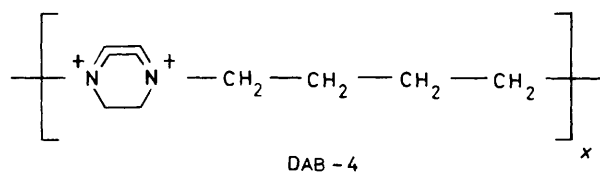


Figure 1. Magic-angle spinning ^{13}C n.m.r. spectra of solid DAB-4Br polymer (lower trace) and the DAB-4-containing gmelinite (upper trace).

Here, we extend the use of the DAB-4 polymer in syntheses where aluminium is not intentionally added to the gel. Two gels were used: (i) $0.8 \text{ R} \cdot 1.0 \text{ Na}_2\text{O} \cdot 10 \text{ SiO}_2 \cdot 365 \text{ H}_2\text{O}$ and (ii) $0.5 \text{ R} \cdot 0.45 \text{ K}_2\text{O} \cdot 7.5 \text{ SiO}_2 \cdot 325 \text{ H}_2\text{O}$, where R represents the DAB-4 unit illustrated above. Starting materials included NaOH, KOH, Ludox-HS40, and DAB-4OH. DAB-4OH was prepared by passing an aqueous solution of DAB-4Br through a Br^-/OH^- anion exchange column. The ^{13}C n.m.r. spectrum of this solution (pH 13–14) was the same as that for DAB-4Br in water. The gels were heated in Teflon-lined autoclaves at autogenous pressures at 150°C for 6–7 days. In both cases ZSM-12 was obtained. Again a 12 membered ring structure is formed with the use of the DAB-4 polymer. In the absence of DAB-4OH no molecular sieve materials were crystallized. Thus, a true templating effect is observed. The ZSM-12 product was identified by its X-ray powder diffraction pattern and mid-i.r. spectrum by comparison with published data.⁶ No appreciable differences (other than morphological ones) were noticed between the two samples of ZSM-12. The particles obtained from the gel containing Na_2O were approximately $2 \mu\text{m}$ in length and $0.5 \mu\text{m}$ in diameter with morphology similar to that illustrated previously for ZSM-12 (ref. 7, Figure 9), while the product from the synthesis with K_2O -containing gel included particles of approximately $10 \mu\text{m}$ in length and $1 \mu\text{m}$ in diameter with morphology similar to that illustrated in Figure 4 of ref. 7.

The m.a.s. ^{13}C n.m.r. spectrum of the ZSM-12 sample prepared with Na_2O was similar to the upper trace of the figure except that the peaks at δ 52.9 and 45.3 were approximately equal in intensity. Thus, the DAB-4 polymer is incorporated into the channel system of ZSM-12. ZSM-12 possesses a monoclinic unit cell with $a = 24.88$, $b = 5.02$, $c = 12.15 \text{ \AA}$, and $\beta = 107.7^\circ$, and contains 28 tetrahedral atoms.⁸ Bulk chemical analysis of the ZSM-12 reveals that $\text{SiO}_2/\text{Al}_2\text{O}_3$ 555, Na/unit cell 0.65, N/unit cell 2.66, C/unit cell 11.8, and

C/N 4.5. Therefore, there appears to be approximately one repeat unit of the polymer per unit cell.

These results illustrate the templating effect of the DAB-4 cationic polymer in the synthesis of zeolites. The polymer can be employed over a substantially large composition range: gmelinite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ 5–7),⁵ mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ~20),⁵ and ZSM-12 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ~550), and in each case, a 12 membered ring, noninterpenetrating channel system is obtained in which the DAB-4 polymer is accommodated.

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