

Resolving Sites of Occupancy of Tetramethylammonium Ions in Zeolites using ^{13}C N.M.R. Spectroscopy

Richard H. Jarman*† and Michael T. Melchior

Exxon Research and Engineering Company, Clinton Township, Route 22, Annandale, New Jersey 08801, U.S.A.

Isotropic ^{13}C n.m.r. chemical shifts distinguish between tetramethylammonium ions trapped in the α and β cages of the zeolite A structure and are insensitive to Si:Al ratio; the observed intensities indicate near complete occupancy of the β cage over the complete composition range.

It has been concluded from observations of splittings in the methyl resonances in high-resolution ^{13}C n.m.r. spectra of tetrapropylammonium^{1,2} and tetrabutylammonium² ions, contained in zeolites ZSM-5 and ZSM-11 respectively, that the chemical shifts of these carbon atoms are sensitive to their location in the zeolite. In this paper we demonstrate the particular sensitivity of the ^{13}C n.m.r. chemical shift of the methyl carbon atoms in tetramethylammonium (TMA) ion to the cage environment of the zeolite in which it becomes trapped during crystallization from an alumino-silicate gel. The results illustrate the templating role of the TMA cation in the formation of the zeolites concerned, and further demonstrate the application of high-resolution ^{13}C n.m.r. spectroscopy as a structural probe for zeolite materials that are prepared in the presence of organic bases.

The zeolites studied are two with structures based on the sodalite (β) cage: the A-type zeolite, ZK4,³ and the high silica analogue of sodalite, TMA-sodalite. The A structure consists of a cubic array of β cages linked through double 4-rings which enclose polyhedral α cages.⁴ The sodalite structure consists of

a dense, space-filling array of β cages fused at all 6-ring and 4-ring faces.⁵

The synthesis of these materials from alumino-silicate gels containing the TMA cation, and their characterization by high resolution ^{29}Si n.m.r. spectroscopy and powder X-ray diffraction have been described previously.⁶⁻⁸ Cross-polarization (c.p.) ^{13}C n.m.r. spectra were obtained at 50.2 MHz on a JEOL FX-200 WBS spectrometer operating at 4.7 T, using a Chemagnetics magic-angle spinning (m.a.s.) probe. The corresponding ^1H frequency was 200 MHz. Sample spinning rotors were composed of Delrin. To suppress the Delrin resonance, and associated side-bands, advantage was taken of the long proton spin-lattice relaxation time of the rotor material compared to the sample by applying a 180° proton inverting pulse followed by a delay prior to the spin-lock c.p. sequence.⁹ With a delay of 0.5 s the Delrin resonance was near the null point while the sample resonances were largely recovered. A single c.p. contact time of 5 ms was used throughout, with a delay of 4 s.

The spectra of three ZK4 samples, prepared with different Si:Al ratios, and of TMA-sodalite are shown in Figure 1. Chemical shift values are collected in Table 1. The chemical shift of absorption I is identical for the four spectra and is increased (greater shielding) by 2.4 p.p.m. compared to

† Present address: Amoco Research Center, P.O. Box 400, Naperville, Illinois 60566, U.S.A.

aqueous TMA cation. Since peak I in the spectrum of TMA-sodalite must correspond to TMA cation contained in the β cage, this peak in the ZK4 spectra is assigned to TMA

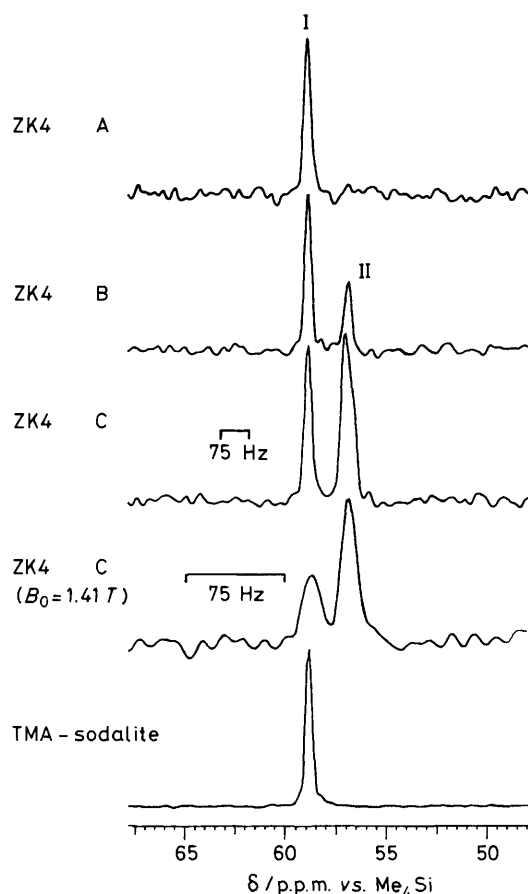


Figure 1. ^{13}C N.m.r. spectra of ZK4 and TMA-sodalite obtained using m.a.s. and single-contact c.p. with proton inversion.

cation in β cages of the A structure. Peak II corresponds to TMA cation contained in the larger α cages.

The total TMA cation contents of the materials were determined by both elemental and thermogravimetric analysis (TGA). The concentrations of TMA cation per unit cell, determined analytically, are compared with the concentrations calculated from the n.m.r. spectra, assuming full occupancy of the β cages, in Table 2. The overall agreement is quite good. Although the higher apparent n.m.r. values for B and C suggest that the β cages in these materials are not completely occupied, this is an artifact of the detection sequence used. The proton T_1 of the α cage TMA cation is somewhat shorter than that of the β , and hence the intensity of the latter is suppressed under the experimental conditions. Lower ratios are obtained by c.p. in the absence of the proton inversion step. The spectra are nearly quantitative at long contact times (10 ms), being similar to spectra detected using a single 90° carbon pulse and a sufficiently long pulse delay (Table 2). The latter are in excellent agreement with the analytical data. Slight differences have been observed in the c.p. dynamics of the two cations, and a detailed account is in preparation.

Support for the above interpretation of the n.m.r. spectra is derived from closer study of the TGA. A maximum at 375°C in the derivative mass loss of C, not observed in that of A, can be associated with decomposition of the less tightly bound α cage TMA cation. Decomposition of the β cage ions occurs at higher temperature, and is similar for the three samples.

The templating role of the TMA cation during crystallization of ZK4 is clearly established by these ^{13}C n.m.r. results. The ion appears to be entirely selective for the β cage in materials containing one TMA cation per unit cell. As the Si:Al ratio of the crystal rises, the β cage remains fully occupied but the total ion content increases, the excess being accommodated in the α cage. These results give considerable substance to the observation that neither ZK4, nor high-silica sodalite can be prepared in the absence of TMA cation.

Sample C contains an average of about 1.2 cations per α cage, implying that at least 20% of the α cages are doubly

Table 1. ^{13}C N.m.r. chemical shift data from Figure 1.

Sample	Si:Al	Sodalite cage composition	Peak I/ δ^a	Peak II/ δ^a
ZK4 A	1.16	$[\text{Al}_{11}\text{Si}_{13}\text{O}_{48}]^{11-}$	58.92(8)	—
ZK4 B	1.62	$[\text{Al}_{9.2}\text{Si}_{14.8}\text{O}_{48}]^{9.2-}$	58.84(8)	56.94(8)
ZK4 C	2.71	$[\text{Al}_{6.5}\text{Si}_{17.5}\text{O}_{48}]^{6.5-}$	58.84(8)	56.97(8)
Sodalite	4.7	$[\text{Al}_{4.2}\text{Si}_{19.8}\text{O}_{48}]^{4.2-}$	58.84(8)	—
TMA ⁺ (aq.)				56.4

^a P.p.m. vs. Me_4Si .

Table 2. Analytical data for the ZK4 and sodalite samples.

Sample	Unit cell	TMA per unit-cell				
		β	α	Elemental ^a	TGA	N.m.r. ^b
ZK4	A	1	1	1.02(1)	1.01(2)	1.00
	B	1	1	1.43(1)	1.38(2)	1.52
						1.45 ^d
					1.37 ^e	
C	1	1	2.18(1)	2.04(2)	2.52	
					2.34 ^d	
					2.15 ^e	
Sodalite	2			^c	1.99(2)	2.00

^a Obtained by subtraction: $\text{Na} + \text{TMA}/\text{Al} = 1$. ^b Assuming peak integration $\int I_\beta \text{d}\nu = 1$. ^c Sodalites tend to be cation rich and contain an excess of anions. ^d Spin-lock c.p.; no proton inversion, contact time = 10 ms. ^e Single 90° carbon pulse; delay of 36 s.

occupied by TMA. The existence of two distinct cage environments appears to be reflected in the ^{13}C n.m.r. spectrum by the shoulder in peak II which is absent from the spectrum of B. The increased width of this peak is confirmed to be a chemical shift effect by observing the spectrum recorded at the lower field of 1.41 T, Figure 1. The width in frequency units of peak II is markedly increased at the higher field, suggesting unresolved chemical shift dispersion, whereas the width of peak I is practically unchanged. The latter's symmetry, narrowness, and insensitivity to applied field imply that the ^{13}C - ^{14}N dipolar interaction is vanishingly small under m.a.s. conditions, which in turn implies that the tetrahedral symmetry of the TMA cation is preserved inside the β cage.¹⁰

In conclusion, isotropic ^{13}C n.m.r. chemical shifts of the methyl carbon atoms of TMA cations are strongly dependent upon the structural nature of their cage environment in a zeolite, and also independent of the chemical composition of that environment. High resolution ^{13}C n.m.r. spectroscopy may therefore act as a probe of the nature of, and distribution

within, the structural units occupied by organic template cations in other zeolite materials.

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