Trimethylsilylation of Zeolites. Evidence for the Presence of Adjacent Aluminium Atoms

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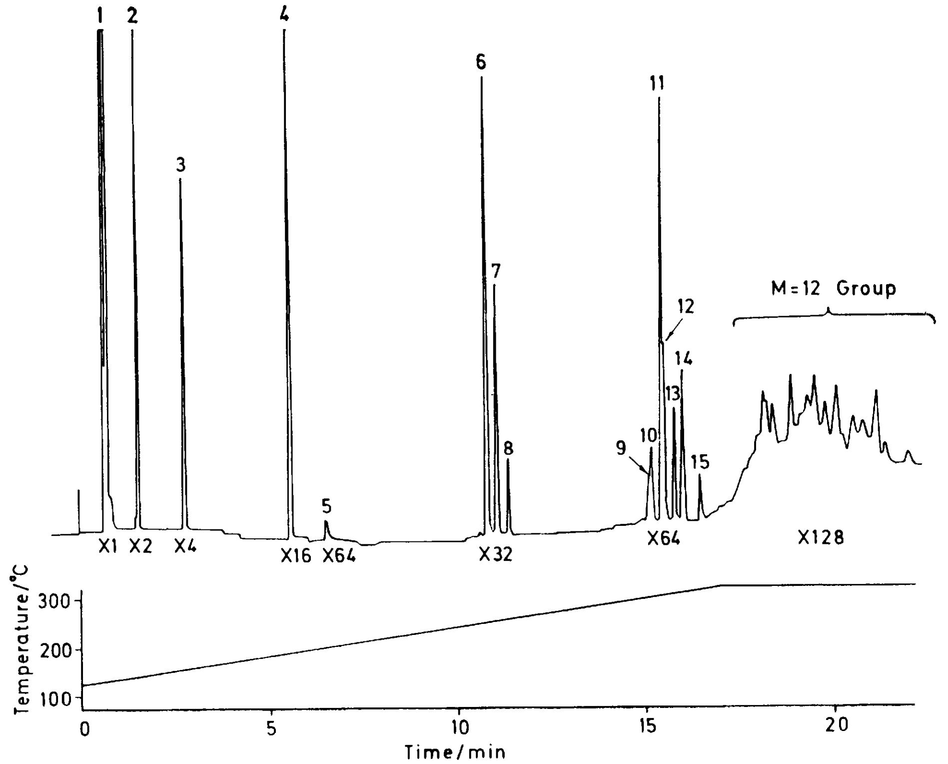
Trimethylsilylation of the zeolites A, ZK-21, P, and X followed by gas–liquid chromatographic analysis of the volatile silicate fragments obtained has produced size-distribution patterns which show that Loewenstein's rule, which forbids adjacent AlO_4 tetrahedra, is not obeyed in these zeolites. Comparison of the results with calculated size distributions for various alternative arrangements of aluminium atoms indicates that in these zeolites between one-third and one-half of the AlO_4 tetrahedra are linked in pairs.

ALTHOUGH the framework structures of most zeolites are known, the exact positions occupied by aluminium atoms in these frameworks have never been established. Since the catalytic properties of zeolites depend upon the presence of aluminium in their structure, it is of considerable importance both in elucidating the mechanisms of zeolite catalysis, and in synthesising more effective zeolite catalysts, to be able to locate the active sites within a zeolite framework with reasonable confidence. In 1954, Loewenstein[1] concluded, from a study of aluminosilicate minerals which did not include any zeolites, that no two AlO_4 tetrahedra could share a common oxygen atom. This rule explained why the minimum silicon : aluminium ratio in a zeolite framework is close to unity, and until recently it has been taken for granted that aluminium and silicon atoms must occupy alternate positions throughout the framework of a zeolite containing equal numbers of each.[2] The validity of Loewenstein's rule as applied to zeolites has been questioned by Engelhardt *et al.*[3] whose ^{29}Si n.m.r. studies of A-type zeolites indicated that the majority of the SiO_4 tetrahedra were attached to three Al and one Si atoms. Lodge *et al.*[4] have also found that the electron diffraction patterns of A-type zeolites are incompatible with the previously accepted structure, and for zeolite A (with Si : Al = 1 : 1) they have proposed a framework in which the linkages between adjacent sodalite cages consist entirely of either Si–O–Si or Al–O–Al bonds. When the Si : Al ratio in a zeolite is significantly greater than one, however, neither the changes in long-range order nor the n.m.r. chemical-shift measurements are likely to be sensitive enough to locate the aluminium atoms with reasonable confidence, and some other technique is required.

Trimethylsilylation has been successfully used to analyse silicate structures,[5-7] and it has been shown[8] that trimethylsilyl derivatives of silicate polyanions containing up to nine silicon atoms can be identified by gas–liquid chromatography. It has also been established[5] that trimethylsilylation of the crystalline aluminosilicates sodalite, natrolite, and laumontite eliminates aluminium from the framework and yields trimethylsilyl derivatives of the remaining silicate fragments; for example, laumontite, which is a zeolite made up entirely of Si_4O_{12}-rings linked through aluminium,[9] gave $[(CH_3)_3Si]_8Si_4O_{12}$ in 81% of the expected amount. This procedure is evidently capable of yielding valuable information about the sizes of the silicate fragments present in the framework of a zeolite, from which it should be possible to deduce the precise locations of the aluminium atoms. Even if the trimethylsilylation reaction brings about further breakdown of some of the larger polyanions, it would nevertheless yield characteristic 'fracture patterns' from which the most likely aluminium locations might be derived, provided that the procedure adopted is designed to eliminate polycondensation reactions that could give rise to larger silicate fragments than were present in the zeolite. For this reason, we adopted the procedure developed by Sharma *et al.*[10] who showed that the polymerisation of silicate anions during trimethylsilylation of soluble silicates could be minimised by employing very low concentrations, *i.e.* using small quantities of solid and relatively large amounts of water in the reaction mixture. The resulting penalty of low yields of the more highly polymerised anions was overcome by the use of an extremely sensitive gas chromatograph.

EXPERIMENTAL

The procedure used was based on that described by Sharma *et al.*[10] The trimethylsilylating reagent was prepared by mixing hexamethyldisiloxane (20 cm^3), Pr^iOH (30 cm^3), water (12.5 cm^3), and hydrochloric acid (15 cm^3 of 12 mol dm^{-3}) at 20—25 °C and stirring for 1 h. The prepared reagent was cooled to 0 °C, and the finely powdered zeolite (0.1—0.3 g, <100 mesh) was added with stirring over 5 min; the cooling bath was then removed, and stirring was continued for 3—4 h while the temperature rose to ambient. A solution of n-tetradecane in hexamethyldisiloxane (1 cm^3 of 0.065 mol dm^{-3}) was added as an internal standard and the organic layer was separated, washed with water (3 portions of 30 cm^3), and stirred for 19 h with Amberlyst 15 ion-exchange resin (2 g). The clear liquid was decanted and analysed by gas–liquid chromatography, using a model 2151 AC (G) Carlo-Erba gas chromatograph with a glass capillary column (10 m × 0.3 mm bore) coated with silicone rubber (OV1; Phase Separations Ltd.), and a flame ionisation detector. The column temperature was programmed to rise at 10 °C min^{-1} from an initial value of 125 °C to a final value of 300 °C which was then maintained to the end of the chromatogram. A typical chromatogram is shown in the Figure. The identities of the numbered peaks were established as follows: peaks 1, 3, 2, 4, and 8



Chromatograph of the volatile silicate fragments produced by the trimethylsilylation of zeolite P

were identified by injections of hexamethyldisiloxane, the internal standard, and the fully trimethylsilylated derivatives of SiO_4^{4-}, $Si_2O_7^{6-}$, and $Si_8O_{20}^{8-}$, respectively. The last three compounds were obtained by trimethylsilylation of olivine (for the monomer), hemimorphite (for the dimer), and the crystalline tetramethylammonium silicate described by Hoebbel and Wiecker [11] (for the cubic octamer). The identities of peaks 5, 6, and 7 were confirmed by comparison of their retention times with literature values.[12] The rest of the numbered peaks lie within the range of retention times that corresponds to the elution of derivatives containing ten trimethylsilyl groups. Of these, peaks 9 and 13 could be attributed to the trimethylsilyl derivatives of the cyclic $Si_5O_{15}^{10-}$ and the hexacyclic $Si_{10}O_{25}^{10-}$ (pentagonal prism) anions respectively, because they were identical to the smaller and larger of the two main peaks in the chromatogram of the trimethylsilylation products of tetra-n-butylammonium silicate.[13] Similarly, peak 10 was attributed to the tricyclic $Si_7O_{19}^{10-}$ anion because it was identical to the second largest peak (apart from the monomer) in the chromatogram of trimethylsilylated tetramethylammonium silicate.[14] Peaks 14 and 15 are almost certainly the trimethylsilyl derivatives of the two isomeric open-chain $Si_4O_{13}^{10-}$ anions, because in any group of trimethylsilylated anions containing the same number of trimethylsilyl groups, the open-chain anions are always eluted last.[12] The remaining two peaks in this group (11 and 12) were not positively identified, but from their positions in the chromatogram they must be trimethylsilyl derivatives of $Si_6O_{17}^{10-}$ anions. The remaining group of unnumbered peaks consists of derivatives containing 12 trimethylsilyl substituents, and would include the trimethylsilyl derivatives of the three open-chain isomers of the $Si_5O_{16}^{12-}$ anion if present.

The ratio of the response factors for the monomer {*i.e.* $[(CH_3)_3SiO]_4Si$, peak 2} and the internal standard was determined by injecting known mixtures of the pure compounds dissolved in hexamethyldisiloxane. The ratios of the response factors for the rest of the numbered peaks to that of the monomer were calculated from the equation: relative response factor $= 6.33 - 2.22\,R$ (where R is the carbon : silicon ratio in the compound), which was obtained by Garzo *et al.*[15]

RESULTS

Preliminary experiments using the procedure described to analyse samples of olivine gave a maximum of 5% of the recovered silica as the trimethylsilyl derivative of the dimeric anion $Si_2O_7^{6-}$, and no detectable amount of any larger anions. It follows that quantities greater than 5% of fragments containing two or more Si atoms are significant. The results obtained from zeolites A, ZK-21 (a slightly silica-rich A-type zeolite), X, and P are given in Table 1; the amounts of isomers containing the same number of Si atoms have been added together, but the totals for anions with more than five Si atoms are probably incomplete because many of the possible isomers of this size are not included among the identified peaks in the chromatogram. However, a result showing the complete absence of pentameric anions is correct if no fragments containing 12 trimethylsilyl groups are recorded; the noise level on the chromatogram was such that the largest observed deviation from the baseline in the absence of any sample was equivalent to less than 0.01% by weight of any silicate fragment of this size.

Table 1

Distributions of silicate anions obtained by trimethylsilylation of zeolites

		Proportions of anions of stated size, as percentage of total SiO_2 recovered											
Zeolite	Si : Al ratio	Si_1	Si_2	Si_3	Si_4	Si_5	Si_6	Si_7	Si_8	Si_9	Si_{10}	Total anions with charge -12 [a]	Total percentage SiO_2 recovered [b]
A	1.0	66	25	6	2	0	1	0	0	0	0	0	82
ZK-21	1.1	63	27	7	2	0	0	0	0	0	0	0	80
X	1.4	46	13	5	12	0	14	1	1	0	4	3	60
P	1.7	37	2	2	11	0	31	0	3	0	3	10	60

[a] Amounts estimated on the basis of an average C : Si ratio and an average molecular weight for this group. [b] Estimated (approximate) from sum of all peaks in the chromatogram, assuming an average C : Si ratio and average molecular weight for the group with charge -12.

DISCUSSION

Zeolites A *and* ZK-21.—If Loewenstein's rule was obeyed, then from zeolite A with equal numbers of silicon and aluminium atoms only monomeric silicate fragments would be obtained. When the silicon : aluminium ratio is greater than 1 : 1, as in zeolite ZK-21, each additional silicon atom replaces an aluminium atom, so that if there are only slightly more silicon atoms than aluminium atoms, every additional silicon atom must give rise to a fragment derived from the pentameric anion $Si_5O_{16}{}^{12-}$. If the Si : Al ratio is R, the weight percent of trimethylsilyl derivative of this anion that would be obtained is $127\,200(R-1)/[384-264(R-1)]$, for values of R not much greater than 1; *e.g.* for $R = 1.1$, the expected amount of pentamer would be 35%. Even if the recovery of fragments of this size was low, this would have been sufficient to be easily detected.

If, on the other hand, the aluminium atoms were arranged according to the structure proposed by Lodge *et al.*[4] then in zeolite A every silicon atom would be linked, *via* oxygen, to one other silicon, and the only trimethylsilylated fragment found would be that from the dimeric anion $Si_2O_7{}^{6-}$; and from zeolite ZK-21, a mixture of dimer and pentamer would be obtained, since every extra silicon atom in that structure links two pairs of SiO_4 tetrahedra. It is evident from the results in Table 1 that Loewenstein's rule is not obeyed, since the proportion of dimeric fragments obtained from both A-type zeolites is five times greater than the proportion obtained from olivine, and no pentameric fragments were detected. Although the proportion of dimeric fragments is much less than that required by the alternative structure of Lodge *et al.*, the results clearly indicate a framework containing adjacent pairs of AlO_4 tetrahedra. If a fraction x of the AlO_4 tetrahedra in zeolite A are linked in pairs, then the weight percent of dimeric silicate fragments would be $30\,300x/(384-81x)$; this gives $x = 0.30$ for 25% dimer, and $x = 0.38$ for 66% monomer, suggesting that about one-third of the AlO_4 (or SiO_4) tetrahedra are linked in pairs.

Table 2

Calculated distributions of silicate fragments left after removal of aluminium from model zeolite frameworks

Framework type	Fraction of adjacent AlO_4 tetrahedra	Si : Al ratio	Weight percent of fragments containing less than 11 Si atoms									
			Si_1	Si_2	Si_3	Si_4	Si_5	Si_6	Si_7	Si_8	Si_9	Si_{10}
A	0.33	1.1	64	25	4	2	0	2	1	1	0	0
	0.5	1.1	59	15	4	1	8	5	1	2	2	2
	0.67	1.1	28	13	10	8	9	7	7	5	7	6
Faujasite	0.25	1.4	39	13	5	9	0	15	5	4	6	4
	0.5	1.4	48	13	2	11	1	6	3	4	7	7
	0.75	1.4	31	28	2	2	5	21	5	2	2	2
Gismondine	0.25	1.7	56	11	5	4	2	10	5	2	5	2
	0.5	1.7	36	4	5	10	3	27	4	4	4	3
	0.75	1.7	59	11	1	1	10	4	2	2	6	4

Zeolites P *and* X.—In order to calculate the expected distributions of silicate fragments from zeolites of higher Si : Al ratio, models of the three zeolite frameworks concerned were constructed using 192 tetrahedra for each, and the tetrahedra were numbered in serial order using odd numbers to represent SiO_4 and even numbers to represent AlO_4. By numbering each sodalite cage (in the type-A and faujasite frameworks) or each ring of eight tetrahedra (in the gismondine framework) according to Loewenstein's rule, and then rotating alternate cages or rings, different numbers of adjacent pairs of AlO_4 tetrahedra could be made to occur at the bridges between the cages or rings. For each such structure, a connection matrix was constructed showing the serial numbers of the four other tetrahedra to which each one was linked. The tetrahedra at the boundaries of the framework were assumed to be joined to the appropriate tetrahedra at the opposite boundary, so as to simulate an infinite network. A computer program was then used to carry out the following operations: for any chosen Si : Al ratio, the requisite number of nonrepeating random even integers was generated and the tetrahedra with these serial numbers were designated as SiO_4; all the remaining even-numbered tetrahedra were deleted, and the numbers of all the continuous segments left of each length from 1 to 10 tetrahedra were counted. This process was repeated as many times as necessary and the segment counts accumulated to give a frequency distribution. Preliminary trials showed that runs of 1 000 repetitions each gave distributions differing by less than one unit in the calculated percentage of any segment up to 10 Si atoms long. Accordingly, all the results were based on 1 000 repetitions. In the type-A framework, each sodalite cage is joined to six others, and the possible fractions of adjacent AlO_4 tetrahedra are therefore (apart from zero and unity) one-third, one-half, and two-thirds; in the faujasite and gismondine frameworks, however, each cage or ring is joined to only four others, so that the possible fractions are one-quarter, one-half, and three-quarters. Each of these possibilities was tested over a range of Si : Al ratios, and the most significant results are given in Table 2. Although the predicted distributions differ from the experimental results in individual frequency values, the overall pattern of the distributions indicates that in all these zeolites, between one-third and one-half of the AlO_4 tetrahedra must be linked in adjacent pairs.

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