

Structural and Catalytic Consequences of Isomorphous Substitution of Silicon by Aluminium and *vice versa* in the Framework of Pentasil Zeolites

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Zeolite ZSM-5 was dealuminated to give material catalytically and structurally identical with silicalite; conversely Si → Al substitution was achieved in silicalite after completion of synthesis to produce ZSM-5 of high aluminium content.

Zeolite ZSM-5,^{1,2} a powerful Brønsted acid catalyst for a variety of chemical reactions, is isomorphous with silicalite,^{3,4} nominally a crystalline form of silica. Silicalite is not a catalyst but it is hydrophobic and organophilic and can remove from water a variety of dissolved organic compounds. It is of considerable interest to be able to control and modify the aluminium content in the silicalite/ZSM-5 substitutional series thereby altering the catalytic, ion-exchange, and sorptive properties of the products. It would be particularly useful to alter Al content *after* the completion of synthesis. We report that this can be achieved in *both* directions (starting from the siliceous or the aluminous end member) and that intermediate Si,Al compositions are also accessible.

The parent zeolite ZSM-5 was synthesised in the usual manner,¹ calcined in air at 500 °C, subjected to two-fold ion exchange with aqueous 1M-NH₄Cl, washed, and dried giving sample 1 with Si/Al = 47.6 (by wet chemical analysis). Sample 2 was prepared by two-fold steaming of sample 1 at 540 °C for 2 h each time followed by extraction with 2M-HCl under reflux, washing and drying. It had Si/Al > 400.

Silicalite was synthesised³ from a reaction mixture composed of 60 g of Ludox AS-40 colloidal silica and 60 g of aqueous 20% tetrapropylammonium hydroxide. The product was washed, dried, and calcined at 600 °C giving sample 3, with Si/Al = 563 as determined by X-ray fluorescence (XRF) and atomic absorption (AA). Aluminated silicalite was prepared^{5,6} by stirring 10 g of sample 3 with 500 ml of 1M-potassium aluminate, prepared by dissolving Al(OH)₃ in a

slight excess of aqueous KOH to pH 12.5. Aluminations was performed at 30 °C for 24 h, whereupon the solid was filtered off, washed, and dried to give sample 4, with Si/Al = 21.6. Powder X-ray diffraction patterns (see Figure 1) show that all samples are highly crystalline. Samples 1 and 4 are orthorhombic, which is typical of zeolite ZSM-5, while samples 2 and 3 are monoclinic at room temperature, characteristic of high-purity silicalite.^{7,8} A decrease in Al content is accompanied by a very slight shift of XRD peaks to higher 2θ values (corresponding to the contraction of the unit cell).

²⁷Al magic-angle-spinning (m.a.s.) n.m.r. spectra given in Figure 2 on the absolute intensity scale show that zeolite ZSM-5 (sample 1) and aluminated silicalite (sample 4) contain substantial amounts of tetrahedrally co-ordinated aluminium, sample 2 contains small amounts of both tetrahedral and octahedral Al, and sample 3 contains only traces of tetrahedral Al introduced as an impurity in silica used for the synthesis.⁹ The spectra were acquired using very short and powerful radiofrequency pulses necessary for the quantitative determination of quadrupolar nuclei.¹⁰⁻¹² Spectral intensities are consistent with the results of elemental analysis and were additionally confirmed by comparison with spectra of samples of known composition. The chemical shift of the signal from

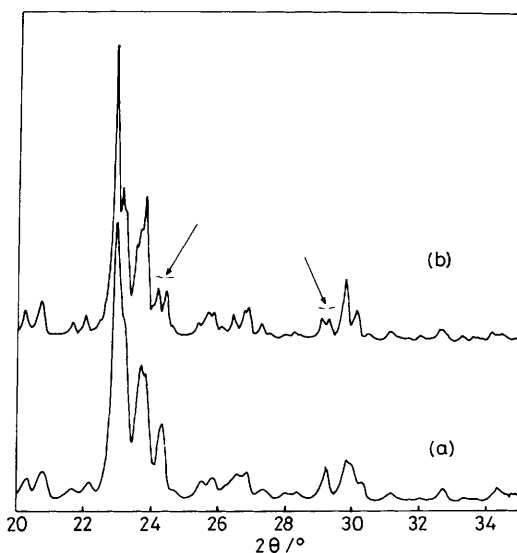


Figure 1. X-Ray diffraction patterns of (a) sample 1 and (b) sample 2; the patterns of samples 3 and 4 are identical with those shown in (b) and (a), respectively.

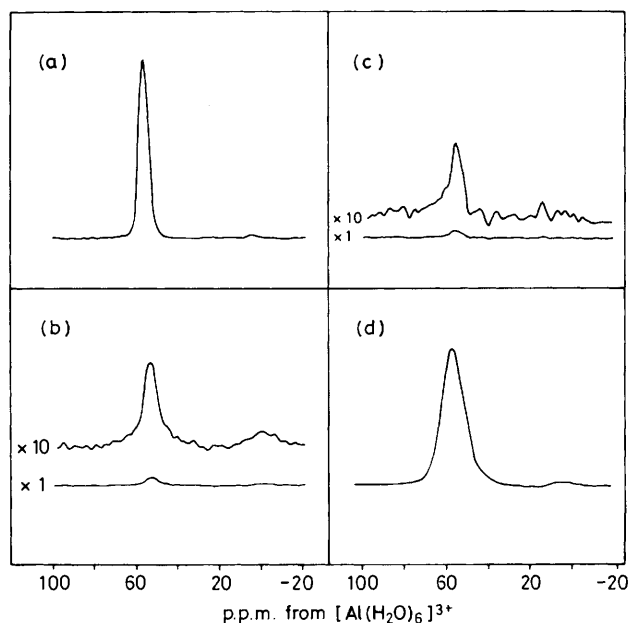


Figure 2. ²⁷Al M.a.s. n.m.r. spectra measured at 104.22 MHz using a Bruker MSL-400 multinuclear spectrometer. Samples were spun in air at 5.2 kHz. Very short (0.5 μs) resonant pulses (90° pulse length 6.3 μs) were applied with 0.5 s recycle delay; 4000 scans were acquired. (a) Sample 1; (b) sample 2; (c) sample 3; (d) sample 4.

Table 1. Total conversion for several catalytic reactions (720 K; 1.2 atm).

Sample	Total conversion (mol %)			
	Toluene	Ethylbenzene	<i>m</i> -Xylene	<i>o</i> -Xylene
1	18.3	9.4	30.0	26.1
2	2.5	0	1.3	2.1

sample 4 [Figure 2(d)] is 57.5 p.p.m. from $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, characteristic of framework Al in ZSM-5,⁹ although its half-width (1452 Hz) is much greater than that found in ZSM-5 (ca. 600 Hz), indicating that Al in aluminated silicalite is present in a wider range of environments. It appears that isomorphous substitution of Al is less site-selective than its incorporation during synthesis. The presence of fine structure in ²⁷Al m.a.s. spectra of some samples of ZSM-5/silicalite^{9,13} does indeed suggest that Al is preferentially distributed among framework sites. It is clear that samples 1 and 4 are aluminous end-members in the Si,Al substitutional series, and that samples 2 and 3 (which give the familiar^{8,9} highly resolved ²⁹Si m.a.s. n.m.r. spectra) are their purely siliceous equivalents.

Catalytic tests were carried out using a pulsed microreactor coupled to a gas chromatograph with a hot-wire detector. The catalyst was prepared in the form of pellets containing 20 wt. % of inactive filler and mixed with crushed quartz glass, also inactive. Carrier gas was hydrogen flowing at 2 ml s⁻¹; prior to measurements the samples were activated at 450 °C in a stream of hydrogen. Three reactions, known to proceed on Brønsted acid sites¹⁴⁻¹⁸ were monitored: (i) disproportionation of ethylbenzene to benzene and diethylbenzene; (ii) isomerisation of *o*- and *m*-xylenes; (iii) alkylation of toluene by methanol (molar ratio of toluene to methanol = 2 : 1). The results of these tests for samples 1 and 2 are given in Table 1. It is evident that sample 1 is highly active, whereas sample 2 has very low catalytic activity which, in view of its high crystallinity, signifies that the Brønsted acid sites have been effectively removed. This confirms that sample 2 is identical with

silicalite. Samples with intermediate Si,Al substitution have also been prepared.

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