Gallosilicate Zeolites from Porotectosilicate Precursors: the Ready Preparation of Gallo-ZSM-11 from Silicalite-II

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Powder *X*-ray diffractometry, multinuclear magic-angle spinning n.m.r. and i.r. spectroscopy, electron microscopy, and gas adsorption studies establish that silicalite-II (Si/Al *ca.* 1050) undergoes facile substitution of Ga^{3+} for Si^{4+} at tetrahedral sites, with retention of the framework structure, on exposure to aqueous solutions of $NaGaO_2$: the method also works for many other siliceous zeolitic structures.

The isomorphous replacement of Si and Al in the framework of zeolitic structure is a topic of both fundamental and practical importance: many advantageous adsorptive and catalytic properties can be imposed upon a zeolite by controlling the nature and distribution of the tenancy of the tetrahedral sites in these useful solids.[1] In most catalytic preparations used to date, cationic gallium enters, by ion-exchange, the intrazeolite (*i.e.* extra-framework) cavities only. To insert gallium into the framework itself, thereby generating gallosilicate zeolites $\{M_{x/n}$-$[(GaO_2)_x(SiO_2)_y]\cdot mH_2O$ where cations M of valence *n* neutralize the charges on the gallosilicate framework$\}$, it is best to use[2—5] silicate and gallate solutions under appropriate hydrothermal conditions: gallo-sodalite, gallo-faujasite, gallo-L, and gallo-omega may thus be prepared. We have discovered that several silica-rich zeolites (Si/Al ratios ranging from 100 to over 1000) can be readily converted into the corresponding, predominantly gallo-silicate zeolite simply by exposure to an aqueous solution of $NaGaO_2$ under conditions where the anions are[6] thought to be principally $Ga(OH)_4^-$.

We focus here on silicalite-II: the preparation and properties of other gallozeolites will be described in the full paper. Silicalite-II has the same relationship to ZSM-11 as silicalite-I has to ZSM-5; see refs. 7 and 8 for further structural elaboration. Typically, 1 gram of silicalite-II with Si/Al *ca.* 1050 is converted, after exposure to 30 ml of an aqueous alkaline solution containing Ga_2O_3 (0.0278 mol l^{-1}) and NaOH (0.10 mol l^{-1}) for 24 h at 100 °C, into a monophasic solid. The unit cell parameters of the product are $a = 20.19$ and $c = 13.50$ Å which are to be compared with those of the parent, 20.07 and 13.44 Å, the space-group being $I\bar{4}m2$. The *X*-ray diffraction and electron diffraction patterns of the starting and final materials, the ^{29}Si magic-angle spinning n.m.r.[3] spectra, and the adsorption–desorption 'fingerprints' of Xe at 194 K, all point to the production of a crystalline solid. Further proof that Ga has entered the framework comes from the fact that the Ga-rich solid (Si/Ga ratio of 9.83) is more hydrophilic than its precursor as seen from the water absorption frequencies in the i.r. spectrum of the gallosilicate. ^{71}Ga magic-angle spinning n.m.r. spectra[3,9,10] also indicate the presence of only tetrahedrally bonded Ga. The diminished uptake of Xe (at 194 K) and of N_2 (at 77 K) is in line with this interpretation.

These results, together with other characterizing tests: scanning electron microscopy,[11] which showed that the morphology of the parent crystal is retained, and electron-induced *X*-ray emission[12] and chemical analysis by atomic absorption, confirm that a monophasic gallozeolite is produced by reaction under mild conditions at the solid–liquid interface. We have also shown that silicalite-I, as well as many other aluminosilicate zeolites, can be readily converted into gallo-silicate and gallo-aluminosilicate analogues of the parent zeolite. Moreover, by using aqueous solutions of sodium aluminate, re-alumination of many siliceous[13,14] zeolites, and the conversion of gallozeolites into gallo-alumino-zeolites,[15] can also be smoothly effected.

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References

1 R. M. Barrer, 'Hydrothermal Chemistry of Zeolites,' Academic Press, London, 1982, p. 251.
2 J. Selbin and R. B. Mason, *Inorg. Chem.*, 1961, **20**, 222.
3 J. M. Thomas, C. A. Fyfe, G. C. Gobbi, S. Ramdas, and M. W. Anderson, in 'Intrazeolite Chemistry,' eds. G. D. Stucky and F. G. Dwyer, A. C. S. Symposia Series, no. 218, 1983, p. 159.
4 Xu Kuren and Liu Xinsheng, *Acta Chim. Sinica*, 1984, **42**, 227.
5 R. H. Jarman, A. J. Jacobson, and M. T. Melchior; *J. Phys. Chem.*, 1984, **88**, 5748.
6 R. L. Moolenaor, J. C. Evans, and L. D. Mackeever, *J. Phys. Chem.*, 1970, **74**, 3629.
7 D. M. Bibby, N. B. Milestone, and L. P. Aldridge, *Nature (London)*, 1979, **280**, 664.
8 J. M. Thomas and G. R. Millward, *J. Chem. Soc., Chem. Commun.*, 1982, 1380.
9 J. Klinowski, Liu Xinsheng, and J. M. Thomas, unpublished work.
10 J. M. Thomas and J. Klinowski, *Adv. Catal.*, 1985, **33**, in the press.
11 M. W. Anderson, Ph.D. Thesis, University of Cambridge, 1984.
12 (a) M. Beer, R. W. Carpenter, L. Eyring, C. E. Lyman, and J. M. Thomas, *Chem. Eng. News.*, 1981, **59**, 40; (b) J. M. Thomas, D. A. Jefferson, and G. R. Millward, *JEOL News*, 1985, **23E**, 7.
13 M. W. Anderson, J. Klinowski, and Liu Xinsheng, *J. Chem. Soc., Chem. Commun.*, 1984, 1596.
14 R. M. Dessau and G. T. Kerr, *Zeolites*, 1984, **4**, 315; see also C. D. Chang, C. T. W. Chu, J. N. Miale, R. F. Bridger, and R. B. Calvert, *J. Am. Chem. Soc.*, 1984, **106**, 8143.
15 Liu Xinsheng, Ph.D. Thesis, University of Cambridge (to be published, 1986).