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Enrichment of Structural Aluminum at the External Surface of Ultrastable Zeolite-Y

The near-surface composition of zeolites has been determined using a number of different techniques including X-ray photoelectron spectroscopy (XPS) (*1–4*), Auger spectroscopy (*5*), fast atom bombardment mass spectrometry (FABMS) (*6*), and electron microprobe analysis (*7*). Tempere *et al.* (*3*) concluded from XPS data that the outer surface of a variety of zeolites was enriched in silicon; however, a number of other groups using several techniques have found that the Si/Al ratio of most synthetic zeolites is about the same at the surface as it is throughout the crystals (*1, 2, 5, 6*). Exceptions to this observation have been noted for ZSM-5 zeolites for which the superficial concentration depends upon a number of factors including the size of the crystals: generally crystals >5 μm exhibit aluminum enrichment at the surface, but crystals in the range 0.1–0.5 μm may be homogeneous or they may be enriched in silicon at the surface (*4, 7*).

Subsequent treatment of zeolites by steaming and dealumination with inorganic acids, ethylenediaminetetraacetic acid (EDTA), or silicon tetrachloride modify the Si/Al ratio at the surface relative to the bulk (*6*). As one might expect, dealumination processes yield a zeolite which is more depleted in aluminum at the surface than in the bulk. Dealumination with EDTA is particularly effective in removing aluminum from the outermost surface layer. By contrast, steaming produces a zeolite which is enriched in aluminum at the surface, as determined by FABMS (*6*).

The purpose of this study was to explore further the surface Si/Al ratios for ultrastable Y zeolites, not only to determine whether surface enrichment occurs but also to investigate whether the aluminum is present structurally in the zeolite lattice. The latter point is particularly important in catalysis since the acidic properties induced by the aluminum would be quite different; i.e., structural aluminum would tend to promote Brønsted acidity while extraneous aluminum would probably result in Lewis acidity. In addition to differences in the type of acidity, the strength of the acid sites would not be the same. Although the external surface has largely been neglected in more conventional zeolite catalysis it may be that the exterior acid sites play a major role in the cracking of molecules which are much too large to enter the intracrystalline regions of the zeolite.

Ultrastable zeolite-Y (HY_u) was prepared according to the method of Ward (*8*). A 4-g sample of NH_4Y (2 wt% Na_2O) zeolite (Linde Y-62, Lot No. 373856) was steamed for 1 h at 600°C. For a 1-h steam treatment of the zeolite, approximately 100 ml of water was vaporized. After cooling to 25°C the steamed material was placed in 1 liter of a 1 *M* $(NH_4)_2SO_4$ solution, and the resulting slurry was heated to 70°C with stirring for 16 h. Subsequently the sample was recovered by filtration, washed with distilled–deionized water until free of SO_4^{2-} ions, and dried in air at 25°C. Depending on the desired depth of sample bed, a specific amount of this material was added to a porcelain crucible which was then placed in a muffle furnace and heated to 480°C for 1 h.

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Samples prepared from beds ca. 20-mm deep are referred to as "deep-bed" (DB), whereas those derived from ca. 3-mm beds are designated "shallow-bed" (SB). In a modification of this treatment a sample was dehydrated and deamminated under vacuum (VAC) up to 480°C.

The XPS spectra were obtained using a Hewlett–Packard 5950A spectrometer with Al $K\alpha$ X-rays (1486.6 eV). The superficial atomic ratios, $(\mathrm{Si/Al})_s$ and $(\mathrm{Na/Al})_s$ were calculated from the equation

$$\frac{\eta_1}{\eta_2} = \frac{I_1}{I_2} \times \frac{\sigma_2}{\sigma_1}$$

where the peak intensity (area), I, for both elements was normalized to the same number of scans, and the photoionization cross-sections reported by Scofield (*9*) were used. The atomic ratios were calculated using intensity data accumulated from the Si $2s_{1/2}$, Al $2s_{1/2}$, and Na $2s_{1/2}$ spectral lines. The error in the calculation of atomic ratios is estimated to be less than ±20%, although the reproducibility is within ±10%. Prior to loading samples into the instrument the powdered zeolites were pressed into wafers and degassed at 100°C for 2 h.

In order to remove extraneous aluminum from the zeolite and to exchange protons with sodium ions the three ultrastable zeolites indicated in Table 1 were slurried in 100 ml of 0.15 *M* NaOH solution for 1 h at 25°C. After filtration the zeolite was washed with 50 ml of water and air-dried at 25°C. In a separate experiment using a Linde NaY zeolite it was shown that dilute NaOH did not solubilize aluminum from the zeolite framework.

As determined by X-ray diffraction (XRD), the unit cell dimensions of the ultrastable zeolites were contracted 0.12–0.17 Å relative to NH_4Y. This contraction along with increased Si/Al ratios in the samples of HY_u confirms that within the crystallites aluminum had been removed from the framework, which is consistent with evidence presented elsewhere for ultrastable zeolites (*10*). The extent of dealumination ranged from 24% for HY_u (VAC) to 49% for HY_u (SB). The XRD data also indicate that ca. 85% of the crystallinity was retained in the ultrastable zeolites, again relative to an NH_4Y zeolite.

TABLE 1

Superficial and Bulk Atomic Ratios for Ultrastable and NH_4Y Zeolites

Sample	$(\mathrm{Si/Al})_s$	$(\mathrm{Si/Al})_b$	$(\mathrm{Na/Al})_s$	$(\mathrm{Na/Al})_b$
NH_4Y	2.6	2.5	—	—
HY_u (SB)[a]	2.0	5.0	—	—
NaY_u (SB)[b]	3.2	6.8	1.0	1.2
HY_u (DB)	1.2	4.2	—	—
NaY_u (DB)	2.5	5.4	0.74	1.0
HY_u (VAC)	1.5	3.2	—	—
NaY_u (VAC)	2.8	4.3	1.0	0.85

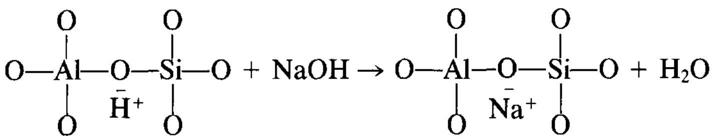
[a] SB, DB, and VAC denote condition used during deammination.

[b] NaY_u obtained by ion exchange of HY_u in 0.15 *M* NaOH.

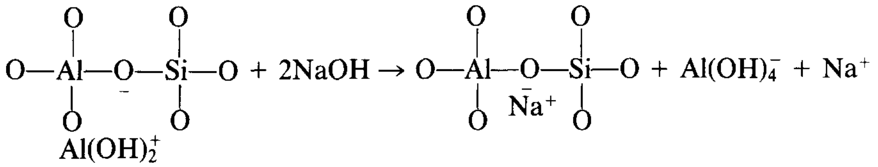
The XPS results are summarized in Table 1. The data for the NH_4Y sample are consistent with other studies which show that the Si/Al ratios on the surface and in the bulk are essentially the same (*1, 2, 5, 6*). By contrast each of the three HY_u samples show Si/Al ratios at the surface which are less than 50% of the values found in the bulk. These results confirm the results of the FABMS experiments which showed that the surface is enriched in aluminum relative to the bulk.

Following treatment of the three ultrastable samples with NaOH two interesting observations can be made. First, up to half of the surface aluminum was removed by this treatment, but even after the removal of extraneous aluminum, both from the surface and the bulk, the value of $(\mathrm{Si/Al})_s$ is still about half of the $(\mathrm{Si/Al})_b$ value. The $(\mathrm{Si/Al})_s$ values indeed approach that of the NH_4Y zeolite. Second, the Na/Al ratios at the surface are approximately unity and are equivalent to the corresponding values found in the bulk, within experimental error. The value of $(\mathrm{Na/Al})_s = 0.74$ for the NaY_u (DB) sample may be attributed to incomplete removal of extraneous aluminum at the surface.

Depending on the forms of aluminum actually present, several reactions may have occurred upon treatment of HY_u with NaOH:



$$\mathrm{O{-}\overset{O}{\underset{O}{Al}}{-}\underset{H^+}{\overset{-}{O}}{-}\overset{O}{\underset{O}{Si}}{-}O + NaOH \rightarrow O{-}\overset{O}{\underset{O}{Al}}{-}\underset{Na^+}{\overset{-}{O}}{-}\overset{O}{\underset{O}{Si}}{-}O + H_2O} \qquad (1)$$



$$\mathrm{O{-}\overset{O}{\underset{\underset{Al(OH)_2^+}{O}}{Al}}{-}\overset{-}{O}{-}\overset{O}{\underset{O}{Si}}{-}O + 2NaOH \rightarrow O{-}\overset{O}{\underset{O}{Al}}{-}\underset{Na^+}{\overset{-}{O}}{-}\overset{O}{\underset{O}{Si}}{-}O + Al(OH)_4^- + Na^+} \qquad (2)$$

$$\mathrm{Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Al(OH)_4^- + 2Na^+} \qquad (3)$$

Equations (1) and (2) were considered on the basis of results obtained by Kerr (*11*), who studied the ion-exchange properties of ultrastable zeolites. Equation (3) is postulated on the assumption that amorphous aluminum was present in the HY_u samples. Regardless of the exact form of aluminum on the surface, the final product from the reaction of HY_u with NaOH would contain Na^+ in the original H^+ or $Al(OH)_2^+$ positions in the zeolite.

The conclusion from this aspect of the work is that a considerable enrichment of structural aluminum occurs near the surface during the process of forming an ultrastable zeolite. The concentration of ion exchange sites and presumably acid sites is greater at the external surface of an ultrastable zeolite than in the bulk. The ion-exchange capacity of the surface suggests that the exterior has remained crystalline and zeolitic, which has been demonstrated recently using electron microscopy (*12*).

Angular distribution measurements (*13*, *14*), which permit a controlled accentuation of the photoelectron intensity from atoms near the surface, indicated no significant changes in $(Si/Al)_s$ ratios for "take-off" angles of 18–58°. The relative areas from the individual atomic levels increased linearly with sin θ, in agreement with theory for a "flat-surface" instrument response function (*15*). Thus, the zeolite wafers used in these XPS experiments exhibited only residual surface roughness (*16*), in contrast to results presented by other investigators (*3*). The constant $(Si/Al)_s$ ratios indicate a uniform atomic composition for depths of 40 Å, the nominal escape depth of excited electrons (*17*).

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REFERENCES

1. Pedersen, L. A., and Lunsford, J. H., *J. Catal.* **61,** 39 (1980).
2. Lunsford, J. H., and Treybig, D. S., *J. Catal.* **68,** 192 (1981).
3. Tempere, J.-Fr., Delafosse, D., and Contour, J. P., *Chem. Phys. Lett.* **33,** 95 (1975); Tempere, J.-Fr., Delafosse, D., and Contour, J. P. *in* "Molecular Sieves—II" (J.R. Katzer, Ed.), Vol. 40, p. 76. Amer. Chem. Soc., Washington, D.C., 1977.
4. Derouane, E. G., Gilson, J. P., Gabelica, Z., Mousty-Desboquoit, C., and Verbist, J., *J. Catal.* **71,** 447 (1981).
5. Suib, S. L., Stucky, G. D., and Blattner, R. J., *J. Catal.* **65,** 174 (1980).
6. Dwyer, J., Fitch, F. R., Machado, F., Qin, G., Smyth, S. M., and Vickerman, J. C., *J. Chem. Soc. Chem. Commun.* 422 (1981); Dwyer, J., Fitch, F. R., Qin, G., and Vickerman, J. C., *J. Phys. Chem.* **86,** 4574 (1982).
7. von Ballmoos, R., and Meier, W. M., *Nature (London)* **289,** 782 (1981).

8. Ward, J. W., U.S. Patent 3,929,672, Dec. 30, 1975.

9. Scofield, J. H., *J. Electron Spectrosc.* **8,** 129 (1976).

10. Haynes, H. W., *Catal. Rev.-Sci. Eng.* **17,** 273 (1978).

11. Kerr, G. T., *J. Catal.* **15,** 200 (1969).

12. Thomas, J. M., *J. Mol. Catal.*, in press.

13. Fadley, C. S., *J. Electron Spectrosc.* **5,** 725 (1974).

14. Fadley, C. S., Baird, R. J., Siekhaus, W., Novakov, T., Bergstrom, S., *J. Electron Spectrosc.* **4,** 93 (1974).

15. Baird, R. J., and Fadley, C. S., *J. Electron Spectros.* **11,** 39 (1977).

16. Fadley, C. S., *Progr. Solid State Chem.* **3,** 843 (1976).

17. Fraser, W. A., Florio, J. V., Delgass, W. N., and Robertson, W.D., *Surf. Sci.* **36,** 661 (1973).

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