The Surface Composition of Dealuminated Zeolites

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Summary Secondary ion mass spectrometry (SIMS) provides a technique for assessing the degree of uniformity in the composition of zeolite crystals; dealumination of faujasite-like zeolites by a steam/acid leaching process produces a more uniform composition than dealumination by ethylenediaminetetra-acetic acid.

THE framework composition of zeolite aluminosilicates is important in determining their physical and catalytic properties.[1,2] Direct synthetic routes to low aluminium forms of many zeolites are not available. Aluminium may, however, be removed by chemical[3] or thermal[4] treatments to give stable crystalline silica-rich products. Where dealumination involves chemical attack at the surface of

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zeolite crystallites the composition of dealuminated products is unlikely to be uniform and this could, particularly, affect correlation between catalytic properties and bulk composition.[2] With this in mind, samples of zeolite Y, dealuminated by both ethylenediaminetetra-acetic acid (EDTA)[3] and steam treatment,[4] were examined by secondary ion mass spectrometry (SIMS), and the results were compared with those for zeolites synthesised with varying composition (Si/Al). Surface species, ejected by argon atoms (3 keV), were analysed by quadrupole mass-spectrometry. After recording the initial spectrum the surface was bombarded for 5 min with an argon ion beam which sputtered off, approximately, the outermost 30 layers. A SIMS spectrum of the resulting etched layer was recorded and the procedure was repeated. Experimental techniques have been described previously.[5,6]

Faujasite-like zeolites (Si/Al between 1·3 and 2·4) were provided by Laporte Industries, mordenite (Zeolon 100) by Norton Chemicals, and ZSM5 was synthesised in these laboratories using published procedures.[7] ZSM5 is one of the more recently synthesised pentasil zeolites. Its unusual pore structure results in considerable shape-selectivity during hydrocarbon transformations. Shape-selective alkylation of toluene, isomerisation of xylene, and production of gasoline from methanol are some of the more important processes proposed for ZSM5 catalysts. Dealuminated zeolites, prepared from NaY or USY,‡ were crystalline and microporous (*X*-ray diffraction and nitrogen sorption) as were the synthesised zeolites.

For the untreated (as synthesised) near-faujasites a plot of surface Si^+/Al^+ (SIMS) against bulk Si/Al (*X*-ray fluorescence) was approximately linear through the origin (slope = *ca.* 0·2), Figure (a). Additionally, composition did not vary greatly with depth of surface layer. The results for synthetic mordenite and ZSM5 were similar to those for synthetic faujasites. The initial values of Si^+/Al^+ were close to values predicted by linear extrapolation from the Figure (a) and surface composition did not change extensively with surface 'etching'. Data in the Figure (b) suggest that the linear correlation in Figure (a) extends over a wide range of composition and is not particularly sensitive to zeolite structure.

For the dealuminated samples (Table), calculated values $(Si/Al)_{calc}$ are estimated from the linear correlation of the Figure. Evidently, dealumination with EDTA causes depletion of Al in the outermost surface layer. Moreover, the ratio Si^+/Al^+ decreases with increasing penetration of the outer surface, which contrasts with the synthesised zeolites used for the Figure. These results suggest that the zeolite crystals dealuminated using EDTA are not homogeneous. Dealumination proceeds from the outside surface producing a composition gradient. An alternative explanation that increased surface Si^+/Al^+ might arise from loss of surface zeolite structure was not supported by an experiment on NaY, calcined to destroy crystallinity (confirmed by *X*-ray diffraction). Conversely, materials dealuminated by steam/acid leaching have values of Si^+/Al^+ closer to those predicted from results for synthetic zeolites (Figure), and changes in surface composition with depth are much less than in samples dealuminated with EDTA. The higher temperatures used in steam treatments presumably permit a more facile 'healing' of dealuminated structures.

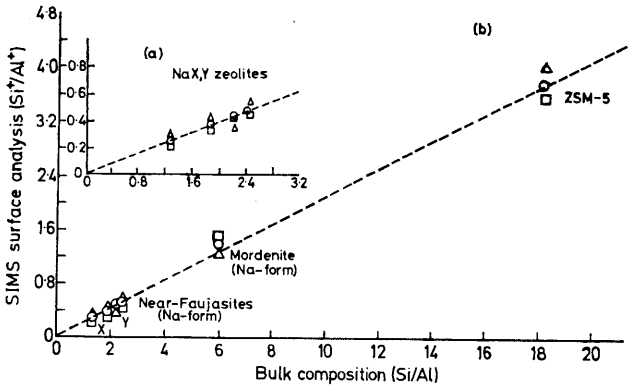

FIGURE. Correlation between SIMS surface analysis and bulk chemical analysis (Si/Al) for synthetic zeolites. △ first layer; ○ after first bombardment; □ after second bombardment.

Comparison of mordenite in the Na- and H-forms (Norton Zeolon 100Na and 100H) suggests that the commercial decationisation results in surface dealumination. Such procedures could provide a means to modify the outer surface composition of zeolite crystals, which could have implications in catalytic selectivity.

Clearly SIMS provides a useful method for the study of compositional variation in zeolites, both for framework and for non-framework[8] species.

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TABLE. Surface composition of dealuminated zeolites.

			First layer		After first bombardment		After second bombardment	
Zeolite	Treatment [a]	Si/Al[b]	$(Si^+/Al^+)^b$	$(Si/Al)^b_{calc.}$	$(Si^+/Al^+)^b$	$(Si/Al)^b_{calc.}$	$(Si^+/Al^+)^b$	$(Si/Al)^b_{calc.}$
Faujasite	i	2·8	1·0	5·0	0·66	3·3	0·58	2·9
,,	i	4·5	3·3	16·5	1·7	8·5	1·7	8·5
,,	i	9·0	11·3	56·5	5·9	29·5	4·2	21·0
,,	ii	6·3	3·0	15·0	2·2	11·0	2·3	11·5
,,	ii	13·9	3·9	19·5	3·5	17·5	3·8	19·0
Mordenite	iii	6·8	11·0	55·0	2·8	14·0	2·6	13·0

[a] i, Dealumination by EDTA; ii, dealumination by steam/acid; iii, decationisation (Norton 100H).
[b] Si/Al, bulk composition; (Si^+/Al^+), experimental values of surface composition; $(Si/Al)_{calc.}$, corresponding calculated 'bulk' composition.

‡ USY is the ultra-stable form of zeolite Y produced by steam treatment.

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