Determination of Framework and Non-framework Aluminium in HY Dealuminated Zeolites by *X*-Ray Photoelectron Spectroscopy

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The surface atomic ratio of framework and non-framework aluminium in a deep bed HY zeolite and in an HY zeolite dealuminated with $SiCl_4$ has been determined by *X*-ray photoelectron spectroscopic measurements.

The catalytic activity of zeolites, especially in the case of bulky reactants, is controlled by the properties of the external surface of the zeolite more than by the global composition of the sample. High-resolution magic-angle spinning solid state ^{29}Si and ^{27}Al n.m.r. spectroscopy has become of major importance in the structural study of zeolites.[1—3] With this technique it is possible not only to determine the different types of silicon atoms and their proportion in the bulk, but also to calculate the average proportion of the framework and non-framework aluminium in the bulk.[1,4] However, it is well known that in zeolite catalysts the composition of the outer surface may differ from that of the bulk.[5] This variation arises during the synthesis[6] and/or by thermal and chemical treatment during activation,[1,6—10] and its occurrence has been demonstrated by surface techniques such as single ion[5] and fast atom bombardment[8] mass spectrometry and *X*-ray photoelectron spectroscopy (x.p.s.).[10,11] The last technique should also be able to provide evidence for the presence of aluminium species in different co-ordination modes. We now report the determination by x.p.s. of the surface composition and the different types of Al surface species in two HY zeolites (deep bed and $SiCl_4$ dealuminated, respectively).

The HY deep bed sample (HYDB) was prepared from an SK-40 (Si/Al 2.4) sample by repeated (×10) ion exchange with aqueous ammonium acetate, followed each time by deep bed calcination at 550 °C in air. The final samples contained <1% of the original Na^+. The HY zeolite dealuminated with $SiCl_4$ (HYDC) was prepared by treating NaY zeolite with $SiCl_4$ under nitrogen at 500 °C, following the procedure described by Beyer and Belenkaya.[12] In order to remove any non-framework aluminium the sample treated with $SiCl_4$ was thoroughly and repeatedly washed[4] with water until Cl^- was no longer present in the water ($AgNO_3$ test). The unit cell constant (a_0) of the resulting zeolites was determined following the procedure described by Fichtner-Schmittler *et al.*[13]

The x.p.s. measurements were made with a Leybold-Heraeus LHS-11 system, using Mg-K_α-excitation (12 kV, 10 mA). The spectra were accumulated with the aid of an HP-1000 computer. The charge effect in the sample surface was compensated for with a low-energy electron-flood gun. The atomic ratio of the elements at the surface was determined by x.p.s. using non-linear background subtraction and integration of the peak areas assuming a Gaussian line shape.

It is well known that deep bed calcination in air of NH_4Y zeolites is accompanied by some degree of framework dealumination. Indeed, in our case the a_0 value (Table 1) is smaller than in the parent NaY sample (a_0 24.70 Å), which indicates that the framework Si/Al ratio has increased from 2.4 for the original NaY zeolite to ~9.0 for the HYDB sample.[13] The extracted aluminium exists as octahedrally co-ordinated

Table 1. Bulk and surface characteristics of the zeolites.[a]

Sample	a_0/Å	Bulk Si/Al	Suface x.p.s., Si/Al_T	Si/Al (1)	Si/Al (2)
HYDB	24.40	9.1	1.9	2.3	10.4
HYDC	24.43	8.0	2.4	2.4	—

[a] Binding energies (in eV) for HYDB (HYDC): Al 2p(1) 75.0 (74.7); Al 2p(2) 73.8 (−); Si 2p 102.7 (102.6).

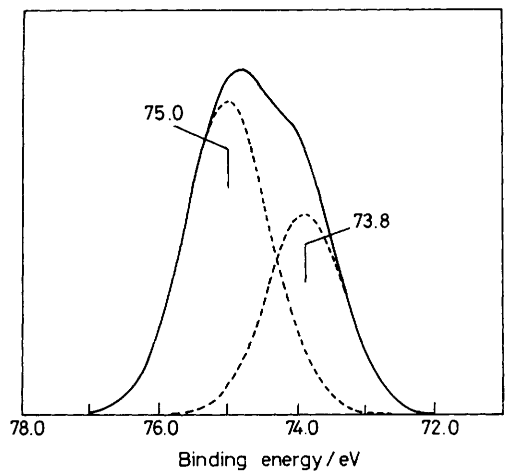

Figure 1. X.p.s. of Al (2p) in a HYDB zeolite.

non-framework species.[1] In the case of the HYDC zeolite the a_0 value indicates that the framework Si/Al ratio is roughly the same (~8.0) as in the HYDB sample. Nevertheless, for the HYDC zeolite the non-framework aluminium was removed by repeated washing of the dealuminated zeolite to eliminate any $AlCl_3$ which could still remain occluded in the sample.[4]

Table 1 gives the binding energies of the Al 2p and Si 2p electrons, relative to the C 1s line taken as 284.6 eV. The Al 2p peaks (Figure 1) were deconvoluted by the method due to Marquardt.[14] The spectra of the Al 2p electrons of the HYDB zeolite (Figure 1) show two aluminium species at higher and lower binding energy, here designated as Al 2p(1) and Al 2p(2), respectively. The x.p.s. results for the HYDC sample showed only the Al 2p(1) species. Since in the HYDC sample most, if not all, of the non-framework aluminium has been extracted,[4] these results show that the Al 2p(1) signal corresponds to framework aluminium while the Al 2p(2) signal must be associated with non-framework aluminium. Furthermore, in the case of HYDB, the Si/Al ratio on the surface is lower than that of the original NaY zeolite, and much lower than the Si/Al ratio in the bulk. Thus, the non-framework aluminium must have migrated to the outer surface of the zeolite, as is supported by the high Si/Al (2) ratio for the surface (Table 1). On the other hand the values of the Si/Al (1) ratio indicate that there should be a gradient in the framework Si/Al ratio in the crystal, this ratio being lower at the surface. A gradient of the same type is also observed (Table 1) for the HYDC sample.

In conclusion, x.p.s. measurements on an HY deep bed dealuminated zeolite shows two aluminium species at 75.0 and 73.8 eV, which can be assigned to framework and non-framework atoms respectively. Moreover migration of the non-framework aluminium to the surface takes place during deep bed calcination of NH_4Y zeolites, the extent of dealumination being higher inside the crystal than in the outer surface.

Received, 19th November 1985; Com. 1636

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