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Determination of the Aluminium Content of the Zeolite ZSM-5 from Peak Positions in the X-Ray Powder Diffraction Pattern

The zeolite ZSM-5 can be synthesised with Al_2O_3 contents ranging from essentially zero up to about 5%. During an investigation into the variation of catalytic activity and product composition with Al content, it became necessary to determine the Al content of ZSM-5 zeolites prepared from a wide range of reaction compositions. However, when the composition of ZSM-5 is determined from a bulk analysis, errors can arise due to the presence of minor phases with chemical compositions differing from that of the zeolite.

It is well known that the lattice parameters of a crystal vary as substitutional impurities are incorporated and that there are resultant changes in peak positions and intensities in the X-ray diffraction powder patterns. These changes can then be used to monitor variations in chemical composition. In the case of zeolites the lattice parameters vary with the degree of Al^{3+} substitution for Si^{4+} (*1*), and also with the counterion and the degree of hydration. In ZSM-5 it has been shown (*2*) that the angular lattice parameter α varies from 90 to 90.6° as the ammonia loading decreases, and also that the Al content may be a factor influencing symmetry changes between apparent orthorhombic and monoclinic symmetry.

In the XRD powder pattern of ZSM-5 we have found that the spacing, Δ, between the two peaks at ca. 45.0 and ca. $45.5°2\theta$ (Cu $K\alpha$ radiation) reduces as the Al content of the zeolite increases. The intensities of these two peaks fall and they broaden considerably as the Al content increases. The precise determination of Δ can be used as a nondestructive method for the determination of the Al content of ZSM-5. It should be noted that absolute peak positions are not required, thus eliminating the need for internal standards.

In order to prepare a calibration curve samples of ZSM-5 were synthesised according to published methods using either tetraethyl- or tetrapropylammonium hydroxide (*3*) or various amines (*4*). Using scanning electron microscopy (SEM) with X-ray microanalysis facilities these samples were carefully examined for evidence of impurities, and any samples containing more than one phase were discarded. After calcination at 600°C in air, to remove organic bases, the selected samples were repeatedly exchanged with 1 *M* NH_4NO_3 solutions until less than 20 μg/g of Na^+ was being exchanged into the solution. These samples were calcined at 600°C to convert them to the H form of the zeolite and then equilibrated at 75% RH. The Al and Si contents of these samples were determined using conventional atomic absorption procedures and were corrected for the absorbed air and water content determined separately by thermogravimetric analysis.

The two peak positions at 2θ values of about 45.0 and 45.5° were determined by scanning over the peak maximum in 0.01° steps, accumulating at least 10^5 counts in each step. This procedure typically takes between 30 and 60 min. These data were then subjected to a 5- or 7-point first derivative convolute (*5*) and the peak maximum was obtained by interpolation. Repeated determinations of Δ showed that it could be determined with an average standard deviation of 0.003° or better. Figure 1 shows that a linear relationship exists between Δ and the Al content of the zeolite. A least-squares fit to the data in Fig. 1 gave the

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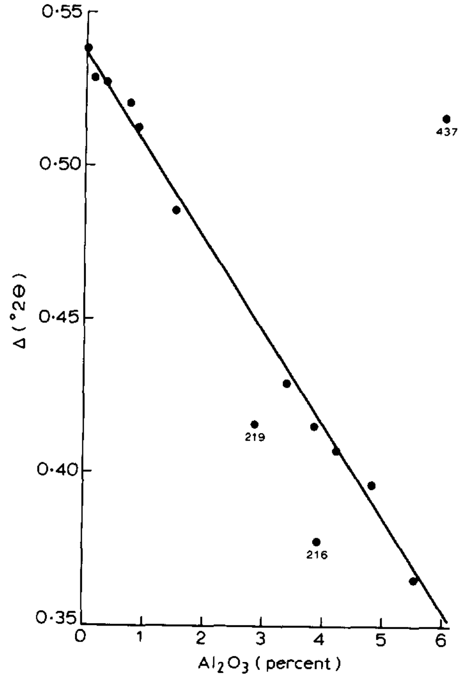

FIG. 1. Peak spacing Δ (°2θ CuKα radiation) versus the bulk Al_2O_3 content (%) of H-ZSM-5 samples equilibrated at 75% relative humidity.

following relationship:

$$\text{percentage } Al_2O_3 = 16.5 - 30.8\,\Delta.$$

Assuming a standard deviation of 0.003° for Δ, the Al content of H-ZSM-5 can be determined to $\pm 0.09\%$.

It is not essential for the ZSM-5 zeolite to be in the H form although the parameters in the above relationship will vary for different counterions. For example, one sample had a value for Δ of 0.417° in the H form, 0.433° in the NH_4 form, and 0.431° in the La form. The preparation of the H form using cold 1 *M* HCl gave the same results for Δ as for the H form prepared by treatment with 1 *M* NH_4NO_3 solutions. However, the effects of treatments with hot, strong acids which could remove a proportion of the Al from the structure have not been investigated.

For ZSM-5 zeolites with high Al contents the peaks in the XRD powder pattern broaden. It is possible that this broadening results from the inhomogeneous distribution (*6*) of Al within individual crystals. The results obtained in this work suggest that any possible effects due to inhomogeneous Al distributions cancel out so that the relationship found above holds up to the maximum Al contents possible.

Figure 1 also shows the utility of the method. Points 216, 219, and 437 do not lie on the calibration line. Examination of these samples by scanning electron microscopy and X-ray microanalysis showed that samples 216 and 219 contained two phases with different Al contents, while sample 437 contained a small amount of an Al-rich phase. No evidence for any of these impurities had been found in previous XRD analysis.

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