I.R. Spectroscopic Evidence for Surface Vibrational Modes formed upon Dehydroxylation of Alumina

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Dehydroxylation of alumina at an activation temperature (T_{ac}) >673 K gives rise to a band in the 1020—1050 cm^{-1} frequency range whose wavenumber and intensity increase with increasing T_{ac} and which is sensitive to $^{16}O \rightarrow {}^{18}O$ exchange and disappears on adsorption of water or bases; it can be assigned to surface vibrational modes of alumina.

Dehydroxylation of metallic oxides produces water by the condensation of hydroxy groups while co-ordinatively unsaturated (c.u.s.) surface oxygen atoms and anion vacancies, exposing c.u.s. metal ions, are created. This may produce considerable strain on the surface, which can lead to new surface vibrational states. On silica, the corresponding vibrational modes have been demonstrated by i.r. spectroscopy: they are characterized by two bands at 908 and 888 cm^{-1},[1] showing that the new surface and subsurface siloxane groups are spectroscopically distinguishable from those characteristic of the bulk.[1,2] On zinc oxide, Zecchina *et al.*[3] showed that the force constants of the bonds present at the surface were appreciably increased with respect to those of the bulk. Morterra[4] noted that pyridine adsorption on highly dehydrated transitional aluminas increased the transparency on the high-frequency side of the alumina cut-off, suggesting that the vibrations of the surface Al–O modes are situated in this region. The same result was obtained when alcohols and thiols were adsorbed.[5] Using a Fourier transform (F.t.)-i.r. spectrometer we have investigated these vibrational modes of alumina, by comparison of the spectra of alumina samples heated at different activation temperatures, T_{ac}.

Alumina powder (Degussa C, surface area 100 ± 10 $m^2\ g^{-1}$) was pressed into the form of a disc (*ca.* 16—20 mg) which was activated by heating under vacuum in a grease free silica cell. I.r. spectra were recorded on a Nicolet FT-MX-1 spectrometer at room temperature.

Figure 1(a) shows the absorption spectrum, in the 1150—950 cm^{-1} range, of an alumina sample activated at T_{ac} 773 and 1173 K. It is clear that the more highly dehydroxylated sample (activated at 1173 K) absorbs more strongly in the 1100—1000 cm^{-1} range. Subtraction of the spectra gives a well-defined band ($\Delta\nu_{\frac{1}{2}}$ 70 cm^{-1}) centred at 1050 cm^{-1} [Figure 1(b)]. Activation at different temperatures allows a more precise study of this feature [Figure 1(c)]: the band appears at 1020 cm^{-1} when T_{ac} is raised from 673 to 773 K. Its wavenumber increases with T_{ac}: 1030 (773 → 873), 1045 (873 → 973), 1055 (973 → 1073), and 1060 cm^{-1} (1073 → 1173 K). The 1050 cm^{-1} band [Figure 1(b)] is therefore a combination of these results.

The same band appears using a starting sample exchanged with deuterium. In another experiment, we exchanged ^{16}OH for ^{18}OH by heating alumina at 773 K under 99% $H_2{}^{18}O$ overnight ($P_{eq.}$ 2×10^3 N m^{-2}). Comparison of the $\nu(OH)$ range of Al_2O_3 heated with $H_2{}^{16}O$ or $H_2{}^{18}O$ and then evacuated at 773 K shows that $^{16}OH \rightarrow {}^{18}OH$ exchange had occurred. Heating the exchanged sample at 1173 K gave a band at 1027 cm^{-1} [Figure 1(b)]; this shift (1050 → 1027 cm^{-1}) due to the $^{16}O \rightarrow {}^{18}O$ exchange shows that oxygen atoms are involved in the vibrational surface modes. If we assume Al–O modes only weakly couple to the lattice vibrations,[6] the ratio of the square roots of the reduced masses is expected to be *ca.* 0.965 (observed value: *ca.* 0.978). Note that the intensity of the 1027 cm^{-1} band [Figure 1(b)] is enhanced relative to the band at 1050 cm^{-1}; this could be due to a stronger overlapping with the bands from the bulk of the sample.

To show that the 1050 cm^{-1} band is due to a surface vibrational mode we introduced successive doses of H_2O to a highly dehydroxylated sample at room temperature: the intensity of the 1050 cm^{-1} band decreases instantaneously and at the same time $\nu(OH)$ modes appear. Bands at 3780 and 3690 cm^{-1} predominate, indicating that they characterize neighbouring OH groups. In another experiment[7] we have shown that the 1050 cm^{-1} band is also sensitive to the adsorption of bases such as pyridine, ammonia, and nitriles. This explains the increase in the transparency of alumina in this range, as already noted by Morterra[4] and Knözinger,[8] on introducing these probes to a highly dehydroxylated sample.

In conclusion it appears that the 1050 cm^{-1} band can be

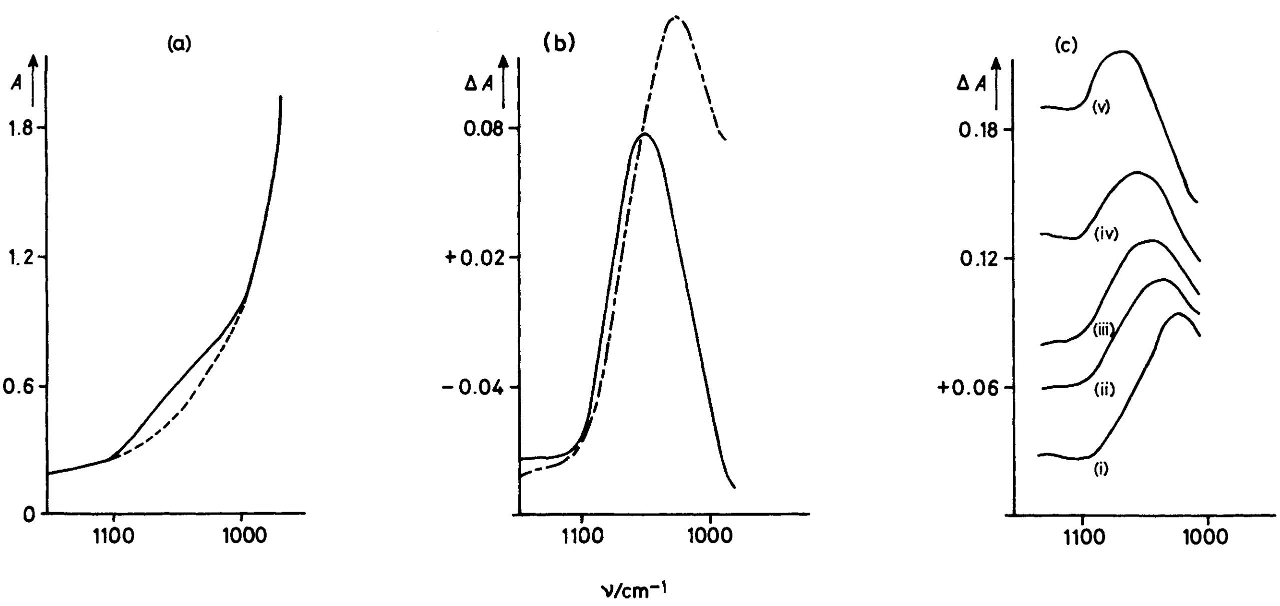
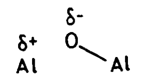


Figure 1. I.r. spectra of an alumina sample. (a) Absorption, ----- activated at 773 K and ——— activated at 1173 K. (b) Difference in absorption (T_{ac} = 1173 K − T_{ac} = 773 K), ——— ^{16}O sample and ·—·—·— exchanged ^{18}O sample. (c) Difference in absorption (^{16}O sample) (i) T_{ac} = 773 − T_{ac} = 673; (ii) T_{ac} = 873 − T_{ac} = 773; (iii) T_{ac} = 973 − T_{ac} = 873; (iv) T_{ac} = 1073 − T_{ac} = 973; (v) T_{ac} = 1173 − T_{ac} = 1073 K.



(I)

assigned to surface vibrational modes appearing on dehydroxylation of alumina. We tentatively assign it to defect modes such as the Al–O mode of the strained groups (I) generated by dehydroxylation. Groups (I) correspond to the active sites for the dissociation of water or acidic molecules.[7] The higher T_{ac} the more strained the groups at the surface and consequently the higher the wavenumber for the corresponding band.

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