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On the Nature of Strong Acidic Brønsted Sites of Amorphous Silica–Aluminas

The problem concerning the nature of Brønsted acidity of amorphous silica–aluminas has been discussed for years but still is not completely solved. From NMR data (*1*, *2*) it follows that the largest fraction of hydrogen of dehydrated silica–aluminas closely resembles that of silica gel. For Houdry M-65 catalyst an upper limit for Brønsted acidity of $<3 \times 10^{13}$ H^+/cm^2 was estimated (*1*). On the other hand, numerous kinetic investigations of catalytic reactions (*3*), titration of the surface with Hammett indicators (*4*), as well as ir spectroscopic studies of adsorption of strong organic bases (*5*) indicate the existence on the surface of silica–aluminas of strong Brønsted acidic sites. Infrared study of hydroxyl groups of these materials perturbed by hydrogen bonding with adsorbed benzene and acetonitrile also reveals the existence of acidic OH groups with pK_a ranging within -4–-8 (*6*).

In our opinion the main reason for failure to detect acidic OH groups of silica–aluminas in ir spectra is their considerably smaller surface concentration and lower thermal stability as compared to those of silanol groups. Therefore the adsorption bands of the acidic hydroxyls in partially dehydroxylated samples are practically undetectable due to intensive background of silanol groups.

In our work highly dehydroxylated powdered samples of amorphous silica–alumina M-46 "Houdry" with Al_2O_3 content of 12 wt% were used. The samples were heated under vacuum at 1070 K and pressure of 10^{-2} N m^{-2} for 2 h. Acidic hydroxyls were regenerated by adsorption of small amounts of H_2O (D_2O) at room temperature. Infrared spectra of OH (OD) groups were measured in diffuse scattered light in the range 2000–4000 cm^{-1} as described in (*7*) using a double-beam ratio recording Perkin–Elmer 580B spectrophotometer and special ir cells supplied with CaF_2 windows.

In Fig. 1 the ir spectrum of pretreated sample (a) and that after adsorption of 5×10^{19} molecules/g of D_2O (b) are shown. The appearance of narrow bands simultaneously in the regions of OH and OD stretching vibrations indicates two processes proceeding on the surface in parallel: H–D exchange between adsorbed molecules of D_2O and remaining silanol groups, and the dissociation of water molecules resulting in the formation of isolated surface hydroxyls. The wavenumbers of stretching vibrations of the newly developed OH (OD) groups are 3610 (2633) and 3650 (2683) cm^{-1} (the band at 2754 cm^{-1} corresponds to Si–OD groups). These hydroxyls are thermally unstable and can be removed from the surface by outgassing the sample at 670 K for 15 min. They reveal strong acidic properties. Indeed they effectively participate in H–D exchange reaction with adsorbed benzene even at room temperature. Moreover, the perturbation of hydroxyls having stretching frequencies of 3610 and 3650 cm^{-1} due to interaction with unsaturated hydrocarbons via H bonding gives rise to significant decrease of their frequencies.

In Figs. 1c and d the spectra of silica–alumina with preadsorbed water after adsorption of benzene and propylene are shown.

In spectrum 1c bands A and B correspond to OH groups with stretching frequencies of 3610 and 3650 cm^{-1} shifted to low frequencies due to H bonding by 350 and 270 cm^{-1}, respectively (band D corre-

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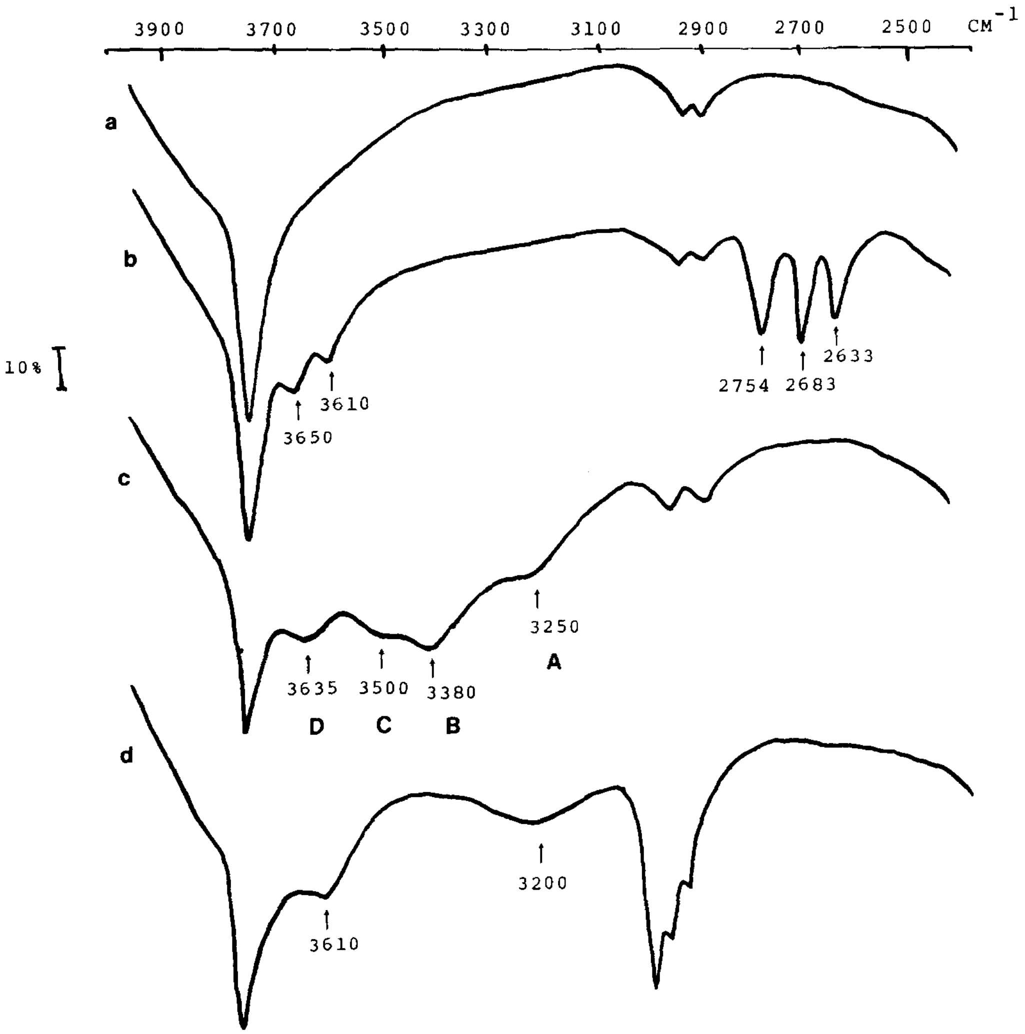

FIG. 1. Infrared spectra in diffuse scattered light of silica–alumina M-46 pretreated at 1070 K for 2 h (a), and after adsorption on its surface of 5 × 10^{19} molecules/g D_2O (b); (c,d)—the spectra of the sample with preadsorbed water after adsorption of benzene and propylene, respectively. Equilibrium pressure of C_6H_6 and C_3H_6 is equal to 2.5 × 10^2 Pa.

sponds to perturbed silanol groups and has a shift of 110 cm^{-1}). The appearance of band C indicates the existence on the surface of silica–alumina of one more type of acidic hydroxyl. Their stretching frequency was found to be equal to 3680 cm^{-1} and it decreases due to interaction with benzene molecules by 180 cm^{-1}. These acidic OH groups, which are more thermally stable than the other acidic hydroxyls, were discussed in (*6*).

After adsorption of proprylene only one broad band at 3200 cm^{-1} (Fig. 1d) was detected, which has to be attributed to OH groups having a stretching frequency of 3650 cm^{-1} perturbed by hydrogen bonding (the shift is equal to 450 cm^{-1}).

Similar acidic hydroxyls are known to exist in zeolites. In H-mordenite they have a stretching frequency of 3610 cm^{-1} which after adsorption of benzene decreases by 350 cm^{-1}. For acidic hydroxyls of zeolite

HNaY with a frequency of 3650 cm^{-1} this shift is equal to 300 cm^{-1}. The broad band at 3200 cm^{-1} was also observed after adsorption of propylene on decationated Y-type zeolites in (*8*) and it was ascribed to acidic hydroxyls interacted via H bonding with adsorbed C_3H_6 molecules.

Thus, there is an obvious similarity between acidic OH groups of amorphous silica–alumina and zeolites. Their amount in silica–alumina is however much lower. For M-46 it is of the order of 5×10^{19} OH/g or only about 1% of the total amount of surface silanol groups.

In conclusion, it should be noted that after adsorption of D_2O the acidic OH groups also can be detected by ir spectroscopy for samples pretreated at lower temperatures, for instance at 770 K. For these samples, however, the corresponding bands are not so pronounced as in Fig. 1b, because the major part of acidic groups likely interacts with neighboring silanol groups via H bonding.

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