IR STUDY OF WATER AND 2-PROPANOL ADSORPTION ON ALUMINA

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The adsorption of water and 2-propanol on alumina has been studied by means of IR spectroscopy. Low temperature adsorption of CO has revealed that evolution of Lewis acid sites begins at 80°C in vacuo when still about 40% of molecular water is present on the surface. The thermodesorption of water proceeds by recombination of neighbouring OH groups. The adsorption of 2-propanol increases the concentration of the nonisolated OH groups and decreases the concentration of isolated ones. The irreversible adsorption influences mostly the C—O and C_β—H bonds in 2-propanol.

The detailed arrangement of hydroxyl groups on alumina is an old problem treated by many authors (see e.g.[1-3]). Concentration and structure of surface sites are decisive for the activity and selectivity of catalysts[4-6]. A model of the surface involving five types of OH groups, from which three are bridged, has been recently proposed by Knözinger and Ratnasamy[2].

Knözinger and coworkers[7-9] had studied the adsorbed species of alcohols on alumina by means of different spectral methods and postulated the bridged alkoxide-like species. Similar conclusion has been drawn from microcalorimetric and FT IR spectroscopic studies of methanol adsorption on alumina by Lorenzelli, Lavalley and their coworkers[10]. The bridged type of alkoxides has been recently found on large number of oxides by FT IR spectroscopy[10-15].

The aim of this study is to gain more information on behaviour of water at thermodesorption and at substitution by 2-propanol, and also to discuss the influence of irreversible adsorption on the bonds in the molecule of 2-propanol.

EXPERIMENTAL

The catalyst used was alumina (Pural SB, Condea) precalcined for 2 h at 600°C. Its specific surface was 206 m²/g. The pellets 2 × 1 cm of surface density 10—14 mg/cm² were used for spectroscopic measurements. For the thermodesorption experiments, the fraction of catalyst 160—350 µm was applied.

2-Propanol (Lachema Brno, purum) was dried by sodium and rectified. Nitrogen (99·9%) deoxygenated and dried by molecular sieve Nalsit 4 Å was used as carrier gas. Its flow rate in the reactor was about 0·75 mmol min⁻¹.

The amount of desorbed water was calculated as a time-integral of its output rate. Its partial pressure in the reactor efluent was determined by gas chromatograph (Gow-Mac model 40−05) on the column 1 m/2 mm, packed by Porapak Q. Deoxygenated and dried hydrogen was used as carrier gas at the temperature of analysis 100°C. The IR cell was made from fused silica to resist large and rapid changes of temperature from −160 to 300°C at the pressure ranges of milipascals.

The placing of catalyst sample in the reactor space allowed to record the spectra at the reaction temperature. The reactants (2-propanol or water) were introduced into the cell by microsyringe through the septum on the top of the cell.

The sample of catalyst was heated for 1 h at 300°C before all experimental runs. The total volume of the cell was about 0.5 l. The volume of reactor itself forms about 20% of the total volume. The spectra were recorded at the reaction temperature and for comparison also at −110°C.

The method of determination of the Lewis acid sites by low-temperature adsorption of CO was described elsewhere[16]. Surface concentration of the molecularly bonded water was determined from the integral of the bands from 1 620 to 1 640 cm^{-1} (see e.g.[17]).

RESULTS AND DISCUSSION

Dehydroxalation of the Surface

There are two principal ways to dehydroxylate the surface of alumina: the first is desorption of water by heating − thermodesorption, and the second is displacement of water, e.g. by alcohols, i.e. the substitution of the OH groups by the OR ones.

Thermodesorption of water. The surface concentration and distribution of hydroxyls depends strongly on activation temperature[1,5,18]. Nine bands of OH groups pointed by the arrows can be seen in Fig. 1. Further bands are supposed in the rather diffusional region 3 000−3 400 cm^{-1}. Their intensity decreases by thermodesorption but their separation improves with increasing temperature. This region of spectra is related to the OH groups in the interaction and then the thermodesorption of water proceeds preferentially by their recombination as can be schematically shown by Eq. (*A*):

$$\text{(A)}$$
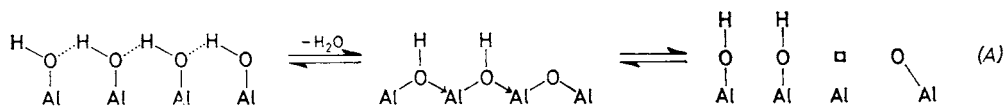
The dehydration of the surface leads to formation of the bridged hydroxyls which are supposed to be in thermodynamic equilibrium with free Lewis sites, which concentration increases almost linearly with temperature, as shown in Fig. 2, while the concentration of the molecularly bonded water decreases to zero at 200°C.

Adsorption of 2-propanol. The adsorption of 2-propanol strongly influences the spectrum of OH groups. The band at 3 770 cm^{-1} almost disappears, while the

intensity of the spectrum in the large region below $3\,700\,\mathrm{cm}^{-1}$ increases (compare lines *1* and *2* in Fig. 3). The effect of adsorption is still more pronounced at $110°C$
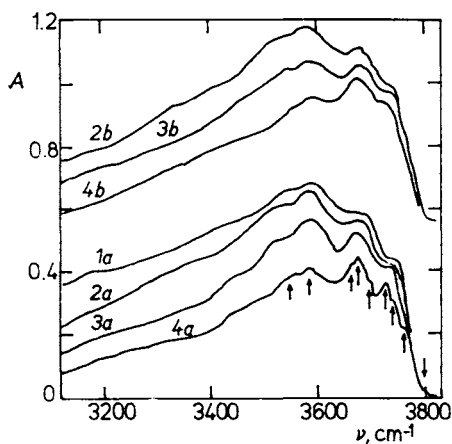

FIG. 1

The spectra of OH groups of alumina at different activation temperatures: *1* 20°C, *2* 110°C, *3* 200°C, *4* 400°C. The series *a* has been measured at −110°C, the series *b* at the activation temperature. The arrows point to the most important individual bands
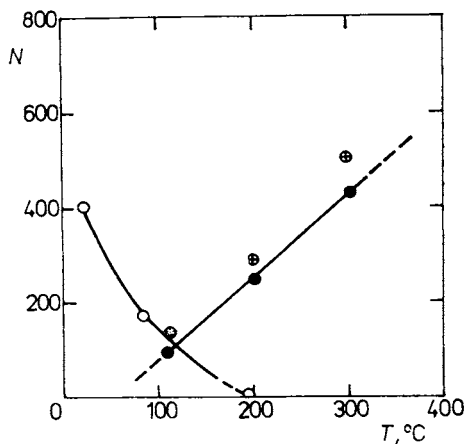
FIG. 2

The temperature dependence of the concentration (N, mmol g^{-1}) of molecular water (from integral of the $1\,620 - 1\,640\,\mathrm{cm}^{-1}$ band) (○), Lewis acid sites (from low-temperature CO adsorption) (●), and the amount of desorbed water by TPD (⊕)
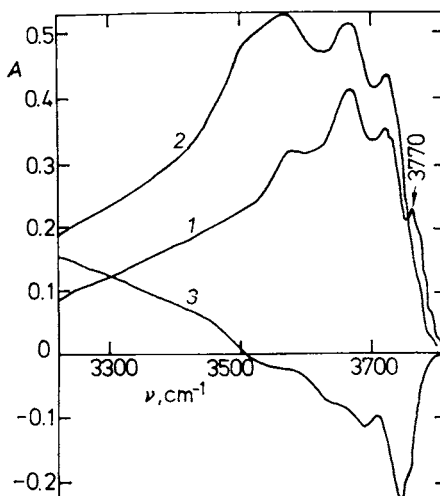
FIG. 3

The spectra of OH groups: *1* after evacuation at 300°C, *2* the first spectrum after adsorption of excess of 2-propanol at 180°C, *3* the differential spectrum before and after adsorption of 2-propanol at 110°C

as the differential spectrum demonstrates (line *3*, Fig. 3). That means that the concentration of isolated OH groups (also the bridged ones) decreases, and the concentration of non-isolated groups increases after 2-propanol adsorption.

The adsorption of some alcohols leads to the substitution of OH groups and displacement of water [19-21], which contains the surface oxygen[20,21]. This is further indirect proof of the interaction of alcohols with the Lewis acid sites. The question of identity of the site for irreversible adsorption and the active sites for dehydration of alcohols will be discussed elsewhere[22]. It seems to be confirmed by good correlation of activity of differently doped aluminas with the concentration of Lewis acid sites before reaction[4]. But the concentration of free Lewis acid sites after adsorption of alcohols or water is too low[23] to ensure the observed steady-state activity. The only explanation of this discrepancy is a bimolecular mutual alcohol–water substitution operating in the steady state as much as in the unsteady state of dehydration reaction of alcohols on alumina (Eq. (*B*)):

FIG. 4

The spectra of 2-propanol: *1* in the adsorbed state, *2* in the liquid phase, *3* in the gaseous phase, *4* after adsorption and 0·5 h of evacuation at 110°C

The first step of the reaction (B) leads to a disappearance of isolated OH groups of type I and formation of non-isolated ones of type II, which is in good agreement with our previously discussed results (see Fig. 3). The second reversible step of Eq. (B) has been described for methanol on thoria in our previous communication[12].

Influence of Adsorption on 2-Propanol Molecule

The bands of irreversibly adsorbed 2-propanol are slightly shifted (Fig. 4). It is worth to compare four spectra in the $1\,000-1\,500\,\text{cm}^{-1}$ and $2\,800-3\,100\,\text{cm}^{-1}$ regions. The first spectrum is of the adsorbed 2-propanol, the second and third ones of liquid and gaseous 2-propanol, respectively, and the fourth spectrum belongs to the catalyst after pumping out the reaction mixture. The most important shift has been observed in the $1\,100-1\,500\,\text{cm}^{-1}$ region, namely the bands at $1\,140$, $1\,500$, $1\,170$, $1\,195\,\text{cm}^{-1}$ which are attributed to the $\nu(\text{C—O})$ vibration of alcohol. A slight shift has been found also in the $2\,850-3\,500\,\text{cm}^{-1}$ region which bands correspond to the $\nu(\text{C—H})$ vibration in the methyl groups.

The comparison of the spectra of methyl groups of 2-propanol in the adsorbed state with those in the liquid and gaseous state demonstrates the similarity of vibration in those groups in the adsorbed and gaseous state characterized by their free rotation.

It can be concluded that the irreversible adsorption affects mostly the C—O and C_β—H bonds of 2-propanol, and the state of the methyl groups of the adsorbed 2-propanol resembles closely that of the gaseous one.

Reactivity of Adsorbed Species

2-Propanol forms stable surface alkoxides and carboxylates characterized by bands at $1\,070-1\,080\,\text{cm}^{-1}$ and $1\,470\,\text{cm}^{-1}$, respectively. These species remain on the surface after evacuation of the reaction cell at the reaction temperature. The alkoxides are removable also by hydrolysis at the reaction temperature or by heating to about $200°C$, while the surface carboxylates remain unchanged even in the presence of water vapour at $300°C$.

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