Infrared Study of Surface Hydroxyl Groups on Zirconium Oxide

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Zirconium oxide has two absorption bands, at 3780 and 3680 cm^{-1}, after several hours' evacuation at 500 °C. The exchange of deuterium with the surface hydroxyl groups was studied by using D_2O, acetone-d_6, 2-propanol-d_8, and chloroform-d. D_2O, acetone-d_6, and 2-propanol-d_8 could completely exchange the hydrogens of the surface hydroxyl groups at room temperature, while chloroform-d could not exchange them even under saturated vapor pressure at room temperature. Hydroxyls showing 3780 cm^{-1} band were selectively and irreversibly chlorinated by chloroform-d. After deuteration, two deuteroxyl bands were observed, at 2780 and 2705 cm^{-1}; these were exchanged rapidly with ammonia and slowly with propylene. At room temperature propylene exchanged the hydrogen with the hydroxyls with a 2780 cm^{-1} band more rapidly than with the hydroxyls with a 2705 cm^{-1} band. In the adsorption and desorption of 2-propanol, the behavior of the 2780 cm^{-1} band was also found to be different from that of the 2705 cm^{-1} band. It was concluded that the 3780 and 3680 cm^{-1} bands could be assigned to surface hydroxyl groups, the nearest neighbors of which have different configurations, and the hydroxyl group of 3780 cm^{-1} is more reactive than the hydroxyl group of 3680 cm^{-1}.

Infrared spectroscopy is one of the most useful methods for the investigation of solid surfaces, and much work has been done on the nature of the hydroxyl groups on various oxides.[1)] The presence of five types of hydroxyl groups on Al_2O_3 was reported by Peri.[2)] The different natures of the five hydroxyl groups were suggested to arise from the difference in their nearest-neighbor configuration.[2)] The two types of hydroxyl groups on SiO_2 were assigned to the surface and the bulk hydroxyls.[3)] The MgO evacuated at 310 °C gave two types of hydroxyls, which were attributed to the surface and the second-layer hydroxyls.[4)] Three types of hydroxyls were observed on CaO and attributed to groups with different circumstances.[5)] Many reports have been reported on the hydroxyl groups on TiO_2, in which the presence of more than two groups has been reported.[6)] The results were explained by Peri's model or a surface model on the (110) plane of rutile.[6c,d)]

We have reported an interesting catalytic action of ZrO_2 toward the preferential production of 1-butene in the dehydration reaction of 2-butanol and the selective formation of *cis*-2-butene in the isomerization of 1-butene.[7)] The results were explained in terms of the basic and acidic nature of this catalyst. The hydrogenation of olefins was also observed[8)] on this oxide at a relatively low reaction temperature (0—50 °C), where hardly no deuterium-exchange reactions took place until the reaction temperature was raised above 200 °C.

In view of the interesting aspects of ZrO_2, we have investigated the nature of hydroxyl groups on the oxide. Tretyakov *et al.*[9)] reported that two kinds of hydroxyls exist on ZrO_2. However, the relative reactivity of the two hydroxyls is not known. The purpose of the present paper is to report the relative reactivity of D_2O, acetone-d_6, 2-propanol-d_8, chloroform-d, ammonia, and propylene.

Experimental

The preparation of ZrO_2 has been described elsewhere.[7)] The D_2O, acetone-d_6, 2-propanol-d_8, and chloroform-d, all supplied by Merck & Co., Inc., were degassed prior to use. The cylinder NH_3 was purified through molecular sieve 3A and sodium metal which was dispersed over quartz wool. Propylene obtained from Takachiho Chem. Ind., Ltd., was used without further purification.

ZrO_2 was ground and pressed into self-supported discs 20 mm in diam under 250 kg/cm^2. The disc was placed in an IR cell and evacuated at the desired temperatures for several hours. Oxygen treatment was applied to burn out organic contamination if necessary. Though it has been reported that oxygen treatment affects the behavior of the surface hydroxyl groups on TiO_2,[6b)] no effect was observed in the case of ZrO_2.

All the spectroscopic measurements were carried out at room temperature by using a JASCO (Japan Spectroscopic Co., Ltd.) DS 701-G double-beam spectrometer. About 50 mg of typical sample discs transmitted about 10% of incident radiation at 4000 cm^{-1} after standard pre-treatment. Ordinate or abscissa scale expansion was applied if it was needed; the reference beam was attenuated for obtaining an appropriate transmittance.

Results

Exchange with D_2O. After several hours' evacuation at 500 °C, ZrO_2 showed two absorption bands, at 3780 and 3680 cm^{-1} (Fig. 1), in agreement with the spectra observed by Tretyakov *et al.*[9)] These bands are characteristic in their narrow and symmetrical contours and have been assigned to hydroxyl groups which hereafter, for the sake of convenience, will be referred to as $(OH)_{I}$ and $(OH)_{II}$ respectively. It is not surprising that the half-width of the $(OH)_{I}$ band is narrow, but it is noteworthy that the other band of a low frequency also has a relatively narrow half-width.

Two or three treatments with 8 mmHg of D_2O at room temperature, followed by evacuation at 500 °C, lead to an almost complete replacement of the original hydroxyl bands with new deuteroxyl bands at 2780 and 2705 cm^{-1}. The former will be referred to as $(OD)_{I}$ and the latter, as $(OD)_{II}$, which correspond to $(OH)_{I}$ and $(OH)_{II}$ respectively. The process of the appearance of these bands is shown in Figs. 1c—1e. The $(OD)_{I}$ begins to appear on evacuation above 200 °C with a decrease in the lower-frequency band at 2705 cm^{-1}. After evacuation above 300 °C, the band at 2705 cm^{-1} decreases markedly in intensity, and two well-resolved bands are obtained at 2780 and 2705 cm^{-1}.

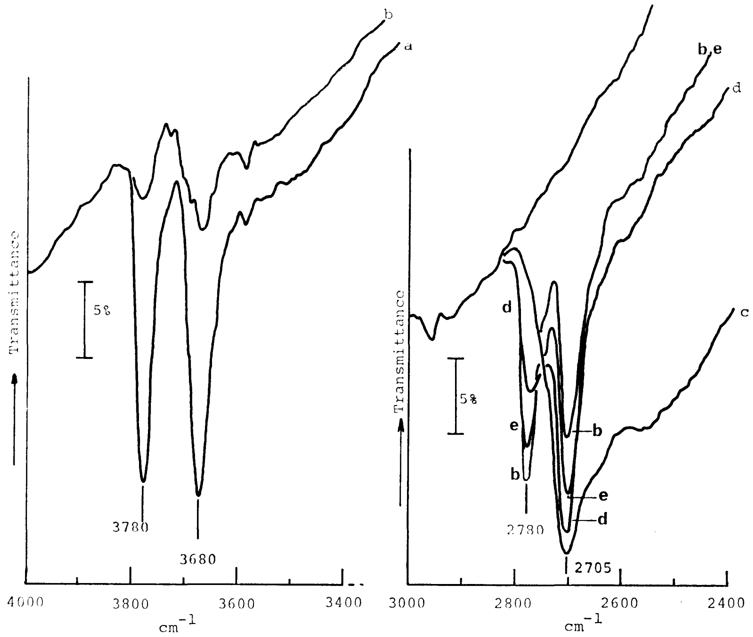

Fig. 1. Exchange of hydroxyl groups with D_2O.
(a) After evacuation at 500 °C for 5 h. (b) Adsorption of 8 mmHg of D_2O at room temperature followed by evacuation at 500 °C for 3 h. (c) Adsorption of 8 mmHg of D_2O at room temperature followed by evacuation at room temperature for 1 h. (d) Evacuation at 200 °C for 1 h. (e) Evacuation at 300 °C for 1 h.

Exchange with Deuterated Organic Compounds. The exchange between deuterated compounds and hydroxyl groups was also examined using acetone-d_6, 2-propanol-d_8, and chloroform-d.

a) Acetone-d_6. The results of the adsorption of acetone-d_6 are shown in Figs. 2 and 3. The adsorption of 1.35 mmHg of acetone-d_6 leads to the complete disappearance of the original OH bands and gives a broad band at 2655 cm^{-1}. The C–D stretching bands are also observed around 2225 cm^{-1}, and C–H bands which could originate from the partial exchange between C–D and hydroxyl groups, appear around 2935 cm^{-1}.

As is shown in Fig. 2, the two bands of $(OH)_I$ and $(OH)_{II}$ were reduced in intensity with an increase in the adsorption pressure of acetone-d_6, keeping their original shapes, while only a broad band appeared around 2700 cm^{-1}, no band of $(OD)_I$ being observed. This indicates that the deuteroxyl groups produced were hydrogen-bonded with each other or with acetone, and that no hydrogen bond was formed in the original hydroxyl groups in the course of adsorption.

During the course of desorption (Fig. 3), the behavior of the two deuteroxyl groups was nearly the same as in the case of D_2O. Evacuation at 200 °C resulted in the production of the $(OD)_I$ band at 2780 cm^{-1}, and above 300 °C two well-resolved bands were obtained, at 2780 and 2710 cm^{-1}.

The spectrum below 2000 cm^{-1} observed at temperatures lower than 200 °C indicates the presence of the formate and the acetate species, the former being assigned by means of the 1589 and 1350 cm^{-1} bands, and the latter, by means of the 1535 and 1440 cm^{-1} bands.[10] Formate species were removed by evacuation above 200 °C, while acetates could not be removed by evacuation up to 500 °C. The acetate species could only be removed by the admission of oxygen and by evacuation at 500 °C.

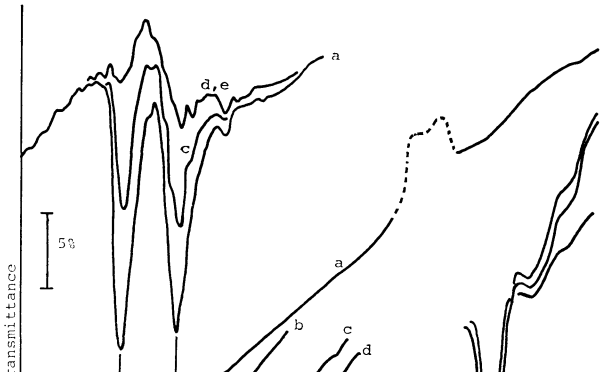

Fig. 2. Adsorption of acetone-d_6.
(a) Background, (b) 0.096 mmHg, (c) 0.23 mmHg, (d) 0.56 mmHg, (e) 1.35 mmHg. Each spectrum was obtained after evacuation at room temperature for 1 h.

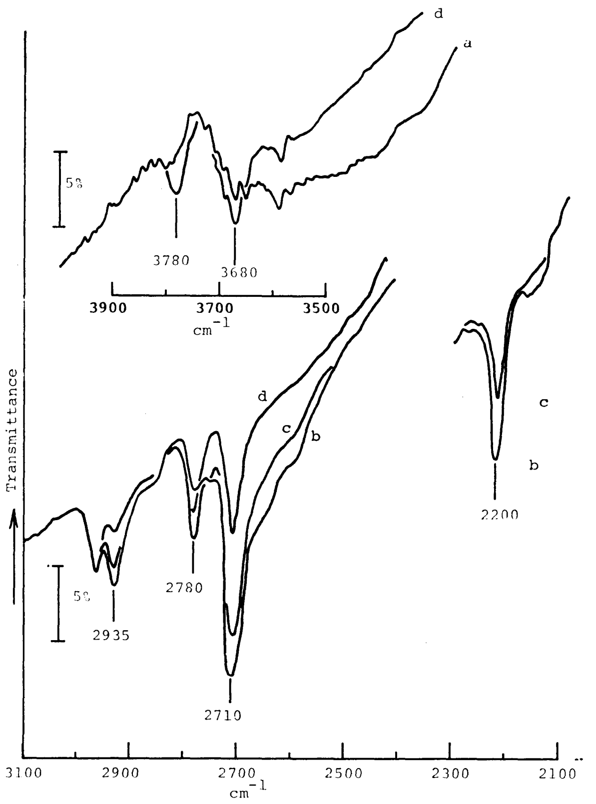

Fig. 3. Desorption of acetone-d_6.
(a) Adsorption of 1.35 mmHg of acetone-d_6 followed by evacuation at room temperature for 1 h. (b) Evacuation at 200 °C. (c) Evacuation at 300 °C. (d) Evacuation at 500 °C.

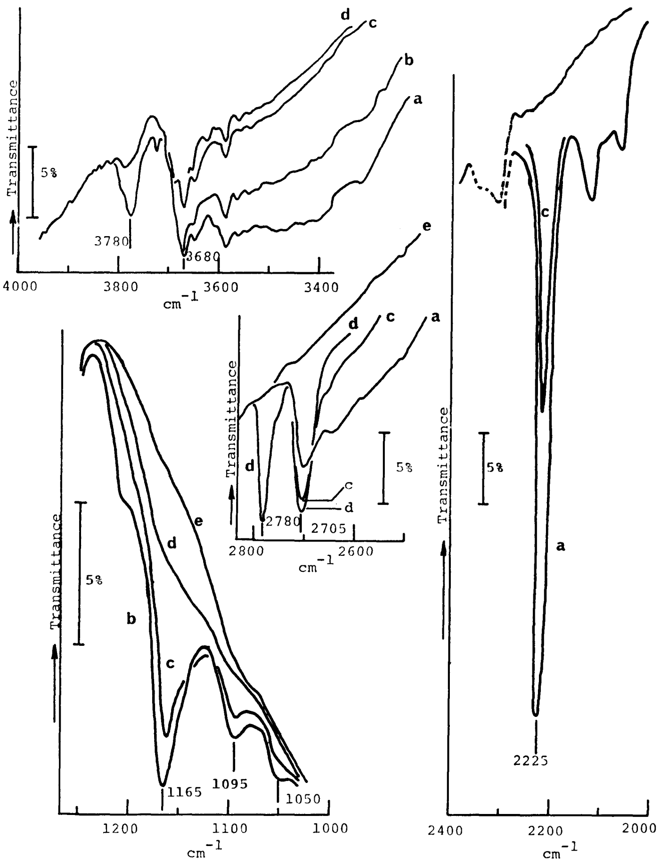

Fig. 4. Adsorption and desorption of 2-propanol-d_8.
(a) Adsorption of 1.32 mmHg of 2-propanol-d_8 followed by evacuation at room temperature for 1 h. (b) Evacuation at 200 °C. (c) Evacuation at 300 °C. (d) Evacuation at 400 °C. (e) Background.

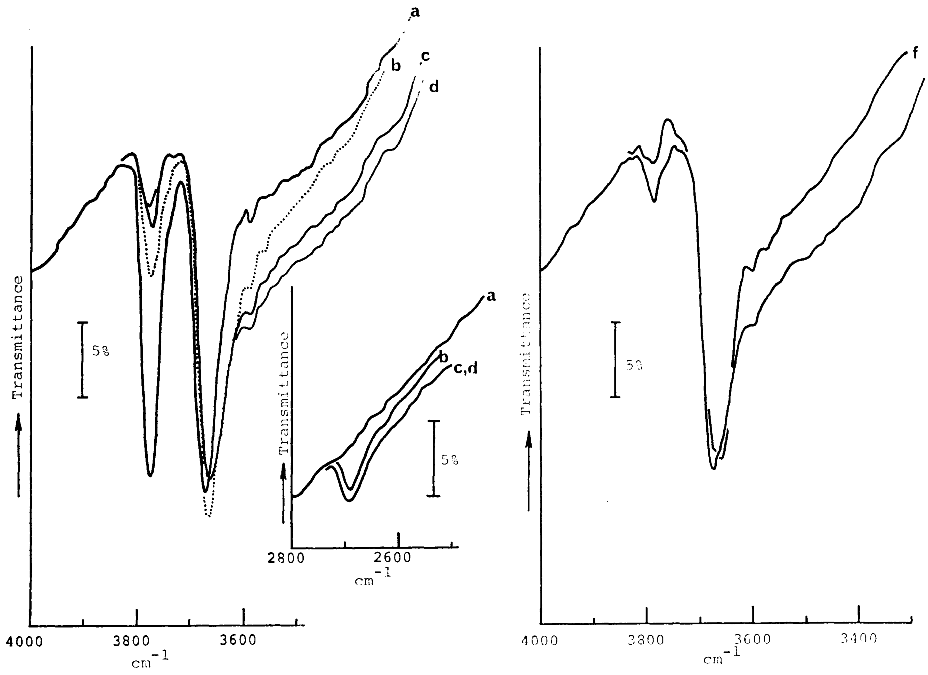

Fig. 5. Adsorption and desorption of chloroform-d.
(a) Background. (b) 0.23 mmHg. (c) 0.56 mmHg. (d) 1.32 mmHg. (e) 3.4 mmHg. Each spectrum was obtained after evacuation at room temperature for 1 h. (f) Evacuation at 400 °C.

b) 2-Propanol-d$_8$. The adsorption of 2-propanol-d_8 at room temperature resulted in the disappearance of two hydroxyl groups and the appearance of a broad band at 2705 cm^{-1}. No marked difference was observed in the behavior of the two hydroxyl bands at 3780 and 3680 cm^{-1} in the course of the adsorption. The observed bands at 2225, 1165, 1095, and 1050 cm^{-1} were assigned to ν_{C-D}, ν_{C-O}, δ_{as}, and δ_s respectively (Fig. 4). Adsorbed alcohol was stable up to 300 °C, and most of these species decomposed between 300 and 400 °C. The composition of the desorbed gas, which was collected and analyzed by means of gas chromatography, was as follows:

Propylene:Alcohol:Acetone=100:10:1.

No indication of the formation of carboxylate species on the surface was obtained.

A difficulty in restoring $(OD)_I$ was observed in the course of the desorption of alcohol. Below 300 °C, there is only one absorption maximum, at 2705 cm^{-1}. The restoration of $(OH)_I$ or $(OD)_I$ was observed above 200 °C in the case of acetone-d_6 or ammonia (which will be discussed later), even if these compounds remained on the surface. This discrepancy can be understood if one assumes that different sites are used for the adsorption of alcohol. 2-Propanol is supposed to adsorb on the sites which produce $(OH)_I$ or $(OD)_I$, when H_2O or D_2O is admitted.

c) Chloroform-d. Since chloroform has been used for characterizing strong and weak basic sites on CaO by comparing the results of benzaldehyde and 2-propanol in terms of the relative ease of the proton abstraction from these molecules,[11] we tried to examine the adsorption of chloroform-*d* on ZrO_2.

The results are shown in Fig. 5. Unlike the cases of D_2O and acetone-d_6 adsorption, the introduction of a small amount of chloroform-*d* leads preferentially to a marked decrease in the $(OH)_I$ band and has little effect on $(OH)_{II}$ except for causing a slight shift to lower frequencies. The $(OH)_I$ almost disappeared after the introduction of 0.56 mmHg of chloroform-*d*, while the 3680 cm^{-1} band kept its intensity. The band broadening at lower frequencies of 3680 cm^{-1} indicates the presence of a hydrogen bond. The formation of new OD bands was quite small compared with the cases of D_2O and acetone-d_6, and no $(OD)_I$ band was observed. Evacuation at elevated temperatures or even the introduction of water vapor do not cause any restoration of the $(OH)_I$ band. On the other hand, though the $(OH)_{II}$ band was extinguished by the adsorption of chloroform at 200 °C, complete restoration was attained by H_2O treatment and evacuation at elevated temperatures.

The production of only a small amount of OD band suggests that hydrogen-deuterium exchange or the abstraction of deuterium by the surface is difficult. Thus, the ZrO_2 surface seems to have only weak basic sites, and the irreversibility of $(OH)_I$ suggests the possible chlorination of $(OH)_I$ by chloroform, though the adsorbed species of chloroform have not been identified.

Exchange with Ammonia and Propylene. The exchange between deuterated surface and ammonia or propylene was also eaxmined. After the deuteration of ZrO_2, ammonia was admitted at room temperature and the changes in the OH and OD bands were recorded. As is shown in Fig. 6, the reduction of the peak intensities in the two OD bands and the formation of an OH band were observed. Again, as in the case of acetone-d_6, the OD bands keep their original shapes, while being reduced in intensity, while the OH band produced shows hydrogen bonding. This indicates a rapid exchange between deuteroxyl groups and ammonia.

Adsorbed ammonia gives absorption bands at 3400, 3350, 1600, and near 1160 cm^{-1}, as is shown in Fig. 7, those bands are assigned to asymmetric and symmetric stretching modes, and to asymmetric and symmetric bending modes, of ammonia respectively. Metal–ammine complexes, such as $[Ni(NH_3)_6]Cl_2$, $[Co(NH_3)_6]Cl_2$, or $[Fe(NH_3)_6]Cl_2$, show deformation bands at about 1600 and near 1160 cm^{-1}, the latter, δ_s, being sensitive to the metal and the environment.[12] The 3400 and 3355 cm^{-1} bands obtained on alumina were assigned to the symmetric and asymmetric stretching vibrations of coordinated ammonia,[12] and the deformation band

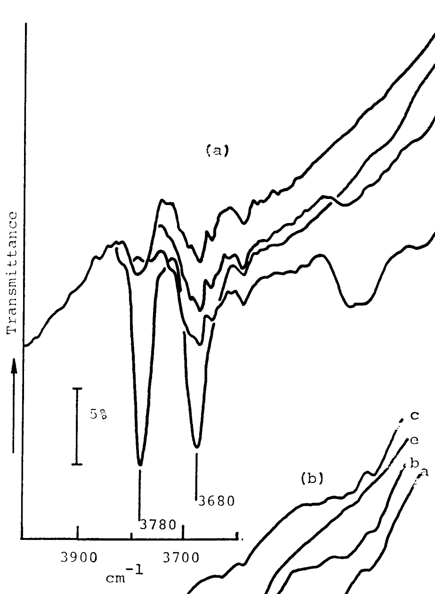

Fig. 6. Adsorption of ammonia on deuterated ZrO_2. (a) After exchange with D_2O. (b) 0.23 mmHg. (c) 0.56 mmHg. (d) 1.35 mmHg. Each spectrum was obtained after evacuation at room temperature for 1 h. (e) Evacuation at 500 °C.

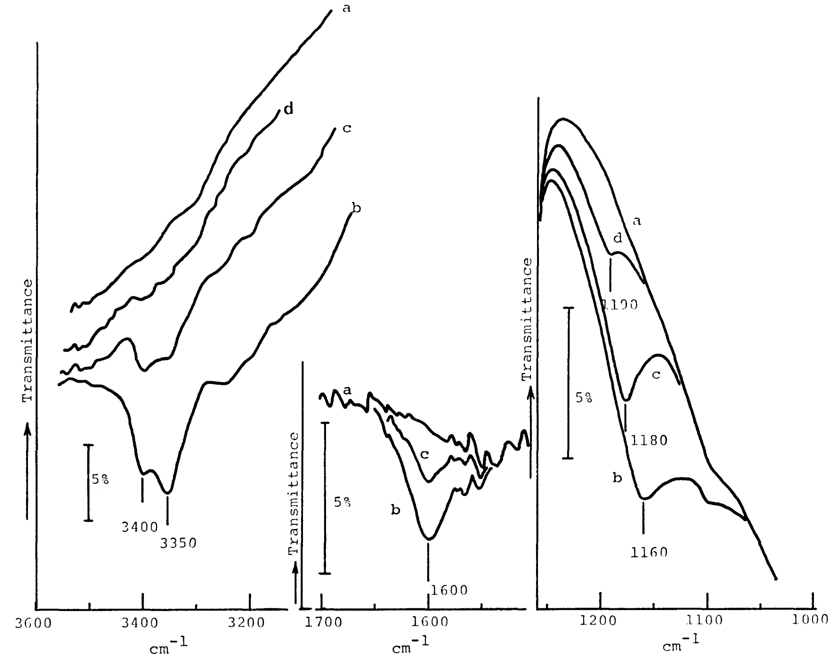

Fig. 7. Adsorption and desorption of ammonia.
(a) Background. (b) Adsorption of 1.35 mmHg of ammonia at room temperature followed by evacuation at room temperature for 1 h. (c) Evacuation at 200 °C. (d) Evacuation at 300 °C.

of coordinated ammonia appeared at 1620 cm^{-1}. Thus, on ZrO_2, the sets of the absorption bands obtained could be assigned to the ammonia coordinated to Lewis acid sites. The peak intensity of a 3350 cm^{-1} band was stronger than that of a 3400 cm^{-1} band when the adsorption pressure was high or the evacuation temperature was low. Thus, hydrogen–bonded species might be involved in the 3350 cm^{-1} band.

The isomerization of butenes took place at 80 °C, and *cis*-2-butene was the major product in the reaction from 1-butene.[7] In this connection, it is interesting to investigate the hydrogen exchanges between olefin molecules and surface hydroxyl groups. An exchange reaction was carried out, using propylene and deuterated ZrO_2, by following spectrometrically the intensity changes in deuteroxyl bands up to 300 °C. About half of the deuteroxyl groups were replaced by exchange in such a period as follows;

Temperature (°C)	r. t.	100	300
Time (h)	20	3	0.5

At higher temperatures, two deuteroxyl bands were reduced in intensity at the same rate, while the 2780 cm^{-1} band was reduced in intensity more rapidly than the 2705 cm^{-1} band at lower temperatures.

Discussion

More than two types of hydroxyl groups have been observed on various metal oxides, such as Al_2O_3,[2] SiO_2,[3] MgO,[4] CaO,[5] and TiO_2.[6] Typical hydroxyl groups on SiO_2[3] were assigned to the surface and the bulk hydroxyls, or to the isolated and the combined ones, on the basis of observations of the deuterium-exchange and particle-size dependencies. Peri has reported that the five types of hydroxyls which are present on the Al_2O_3 surface have different configurations in the nearest neighbors.[2] Because of the very high frequencies observed for the hydrogen–oxygen stretching vibrations of hydroxyl groups on Al_2O_3, Peri regarded them as ions rather than as groups covalently bonded to surface aluminum atoms. More than two kinds of hydroxyls have been observed on TiO_2 by many authors.[6] Parkyns[6d] found two main peaks, at 3728 and 3672 cm^{-1}, with reflections at 3707 and 3636 cm^{-1} on anatase evacuated at 400 °C; he also discussed the models, *i.e.*, the statistical, substitutional, and total hydration models, though he did not assign them individually. The presence of two kinds of hydroxyls (3780 and 3680 cm^{-1}) on rutile was reported by Parfitt,[6c] and these groups were attributed to bridged and terminal hydroxyls, assuming a model for the surface based on the (110) plane on rutile. From the different thermal stabilities of the two bands, the bridged type, $\begin{matrix}M\\M\end{matrix}\!\!>\!OH$, was thought to be more stable because of the bidentate configuration, while the terminal one, M–OH, was considered less stable.

The hydroxyl groups observed on ZrO_2 could be assigned to the surface hydroxyls by taking into consideration the peak shapes and exchange abilities observed in the present work. The assignment of $(OH)_{II}$ to the hydrogen-bonded ones seems to be unlikely because of its relatively narrow and symmetrical shape. We propose to assign two types of bands to the isolated surface hydroxyls which have different neighboring circumstances, *e.g.*, to the bridged and terminal groups, as has been postulated by Parfitt.[6c]

The characteristic behavior of the OH bands which were observed in the adsorption of the materials tested here may be summarized as follows:

1. As is shown in Fig. 2 (acetone-d_6) and Fig. 6 (NH_3), the bands being reduced keep their original shapes, while the produced bands show a strongly hydrogen-bonded nature.
2. The $(OH)_I$ and $(OH)_{II}$ bands show different characters in the cases of alcohol and chloroform adsorption, in which the difficult restoration of $(OH)_I$ was observed during the desorption process.

The first phenomenon can be explained on the basis of a rapid hydrogen exchange between hydroxyls (or deuteroxyls) and adsorbates. When acetone-d_6 interacts with surface hydroxyls, rapid hydrogen-deuterium exchange may take place to form surface deuteroxyl groups, which are observed as a broad band at about 2655 cm^{-1} as a result of hydrogen bonding, while the OH groups which have not interacted with the adsorbate remain unchanged. The adsorption of 2-propanol may be supposed to cause an increase in the concentration of surface hydroxyl groups rather than an exclusive exchange of surface hydroxyl groups with 2-propanol. An increase in the surface hydroxyl groups causes an increase in hydrogen bonding in both the original and produced OH groups. The situation is the same in the case of NH_3, where the hydrogen bond was observed only in the produced hydroxyls, and not in the original deuteroxyls, as a result of the rapid exchange between the NH_3 and the surface OD groups.

The second phenomenon, in which the difficult restoration of the $(OH)_I$ group was observed, can be explained if we assume that alcohol and chloroform are adsorbed exclusively on $(OH)_I$ or $(OD)_I$ sites. As far as alcohol is concerned, the admission of alcohol to ZrO_2 may lead to an interaction only with the surface $(OH)_I$ and to the formation of alkoxyl groups on $(OH)_I$ sites. Such alkoxyl groups are stable up to 300 °C; they decompose to olefin above this temperature.

All the results obtained from the adsorption of chloroform or alcohol and the hydrogen-exchange reaction with propylene at lower temperatures reveal that $(OH)_I$ or $(OD)_I$ is more labile and reactive than $(OH)_{II}$ or $(OD)_{II}$.

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