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Infrared Studies of the Adsorption and the Catalysis of Hydrogen Chloride on Alumina and on Silica

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Catalytic activity of hydrogen chloride on alumina and silica was studied by infrared technique, and it was found that chemisorption of HCl on dry alumina produced new hydrogen bonded OH groups on the surface. Most of these OH groups exchanged with butenes during the isomerization as fast as the rate proportional to the reaction rate. From these facts and the surface acidity of the HCl-treated alumina, it is concluded that the new OH groups produced by the adsorbed HCl are protonic and participate in the *n*-butene isomerization as Brönsted acid. On the other hand, HCl scarcely adsorbed on silica. The isomerization of *n*-butenes on silica did not occur in the presence of gaseous HCl, while OH groups on silica surface exchanged very rapidly with gaseous DCl.

The surface properties of acidic oxides have been studied intensively for many years. On the surface of silica–alumina, an important acidic oxide catalyst, the coexistence of Brönsted acid and Lewis acid sites has been established by the infrared studies of adsorbed pyridine on it (*1*, *2*). However, in spite of many investigations showing the catalytic activity of these acid sites, there have been few attempts to observe the state of the catalyst surface during a reaction. One of the successful experiments was done by Leftin and Hermana (*3*) for *n*-butene isomerization on silica–alumina by the spectroscopic method, in which the catalysis of Lewis acid sites was shown. In respect to the catalysis of Brönsted acid sites, a similar experiment would be possible if a catalyst which has a high concentration of surface protons can be obtained.

On the other hand, some infrared studies of the adsorption of HCl on alumina (*4*), silica (*5*), and silica–alumina (*6*, *7*) were recently reported by Peri. He found that the adsorbed HCl produced new OH groups on the surfaces of alumina and silica–alumina, while HCl scarcely adsorbed on silica. He also reported that HCl-treated silica–alumina had high catalytic activity for polymerization of butenes at room temperature.

If new OH groups produced by adsorbed HCl on alumina and silica–alumina have protonic character and the catalytic activity for Brönsted acid, the adsorbed HCl on oxides could be accepted as a model of surface Brönsted acid.

In the present study, in order to clarify the acid property and the catalysis of HCl in the adsorption state, the adsorption state of HCl on alumina and silica, and also the behavior of the proton on the surface during *n*-butene isomerization were investigated by the infrared technique. The difference of HCl adsorption on both oxides is discussed below in respect to the acid dissociation on the surface.

EXPERIMENTAL METHODS

1. *Materials*

The γ-alumina sample used in this work was the fluffy powder known as Alon C of Degussa Company, having a purity of 99.5% and particle diameter of 5–30 mμ. Its surface area (BET method with nitrogen adsorbate) was 80 m^2/g. The silica

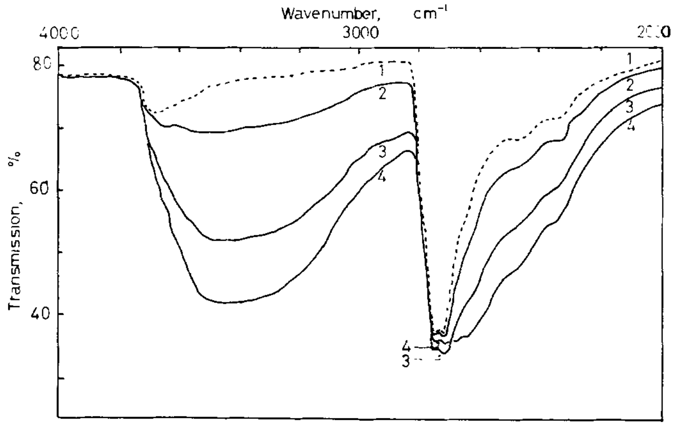

FIG. 1. Spectra of adsorbed HCl on deuterated alumina at room temperature: (1) deuterated alumina evacuated at 500°C; amount (ml; STP) of HCl adsorbed (2) 0.087; (3) 0.21; and (4) 0.34.

sample was obtained from Degussa Company (Aerosil). *n*-Butenes from commercial cylinders (99.7% or better) were used without further purification. The gaseous deuterium chloride (DCl) and HCl were obtained by repeated fractional distillation of deuterochloric acid and hydrochloric acid, respectively, using dry ice and liquid nitrogen traps. The deuterium content in DCl was 99% or higher from infrared analysis.

2. *Procedure*

The alumina and silica samples were mostly used in disks, which were made by spreading oxide powder between two polished steel blocks and compressing under the presssure of 150 kg/cm^2 for alumina and 10 kg/cm^2 for silica for a few minutes. These disks were calcined in air at 500°C for 1 hr and then evacuated for 3 hr in the infrared cell at the same temperature. After these treatments of the disks, gaseous HCl or DCl was admitted to the cell in a small amount while the alumina was held at room temperature, and the infrared spectra were recorded.

When deuterated alumina disks were required, they were repeatedly deuterated with D_2O vapor at room temperature and then evacuated at 500°C in the cell.

The infrared spectra during the 1-butene isomerization were recorded as follows. After the pretreatment and the adsorption of DCl on deuterated alumina, 1-butene was admitted into the cell in a fixed amount and spectra were recorded periodically. Simultaneously, gaseous samples amounting to about 5% of the reaction mixture were removed from the cell and analyzed by gas chromatography using 3 m of alumina column (containing 30 wt % of dimethylformamide) kept at 0°C. The infrared spectra were obtained with a Hitachi type EPI-2 prism spectrometer. All spectra measurements and the reactions were carried out at room temperature.

The surface acidity of HCl-treated alumina (HCl–alumina) was measured by *n*-butylamine titration and spectral measurements of adsorbed pyridine on the catalyst. In the *n*-butylamine titration (*8*), the vessels involved with HCl-alumina were filled with 1 atm of nitrogen gas, which was passed through a charcoal trap kept at −195°C in order to eliminate moisture in the air. The Hammett indicator, dimethylaminoazobenzene ($pK_a = +3.3$), and titer were added into the vessels in fixed amounts and kept at 45–50°C in an air bath for 4 hr, and then the color change of the indicator was observed.

RESULTS

1. *Spectra of Adsorbed HCl on Alumina*

The adsorption rate of HCl on alumina was very rapid and irreversible at room temperature, and the maximum amounts of the adsorption were about 3×10^{14} molecules/cm^2.

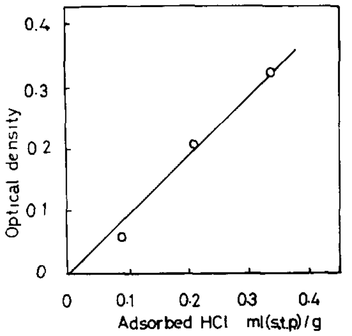

FIG. 2. Relationship of adsorption amounts of HCl with optical density of new OH bands at 3400 cm^{-1}.

The spectra of deuterated alumina and adsorbed HCl on it are shown in Fig. 1. The deuterated alumina showed three absorption bands of 2780, 2740, and 2700 cm^{-1} attributed to the isolated OD groups of the alumina (these bands correspond to the isolated OH bands of 3780, 3730, and 3680 cm^{-1}, respectively). When HCl was adsorbed on the deuterated alumina, growth of the new broad band at around 3400 cm^{-1} was observed. This new band was assigned to the hydrogen bonded OH groups on the surface. The maximum absorbance of this new band was proportional to the adsorption amounts of HCl, as shown in Fig. 2. It is thus seen that almost all adsorbed HCl dissociated on the surface to produce new OH groups, and that the new OH groups interacted with each other, and also with the isolated OD groups originally present, because the isolated OD band at 2700 cm^{-1} decreased with increasing of the broad OH band at 3400 cm^{-1}. These observations are consistent with the results obtained by Peri (*5*).

Since there was a possibility of the formation of water by the reaction of isolated OH groups with adsorbed HCl, as suggested by Peri (*5*), the spectra of the new band produced by the HCl adsorption were compared with the band produced by the adsorption of the water vapor which is shown in Fig. 3. The shape of the OH band due to adsorbed HCl is very different from that of adsorbed water in which there apparently appeared two bands in the OH region of the spectra. Accordingly, it should seem that the new bands in the spectra of adsorbed HCl are not due to the formation of water.

The relative extinction coefficients of the new band and the isolated OH band were estimated from both the intensity of maximum absorption and the number of each OH groups. The number of isolated OH groups on alumina, evacuated at 500°C for 3 hr, was 2×10^{14} OH/cm^2. This value was obtained from the exchange of isolated OH groups with D_2O vapor, where the spectral absorbances of OH groups in initial and equilibrium state were used. The relative extinction coefficient of isolated OH groups at 3700 cm^{-1} was about twofold

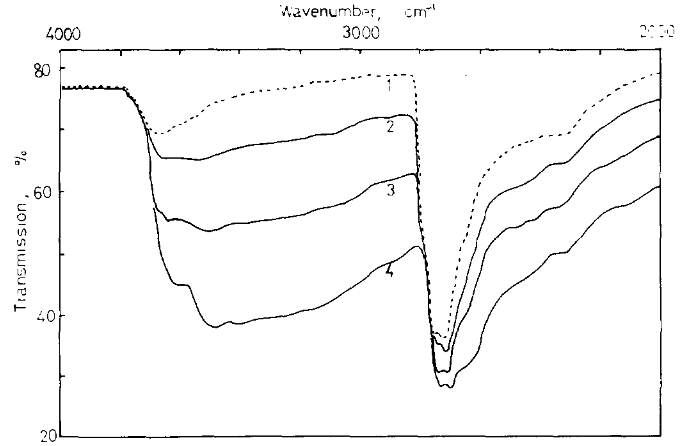

FIG. 3. Spectra of adsorbed water vapor on deuterated alumina: (1) deuterated alumina evacuated at 500°C; amount of H_2O adsorbed (ml; STP): (2) 0.058; (3) 0.11; and (4) 0.24.

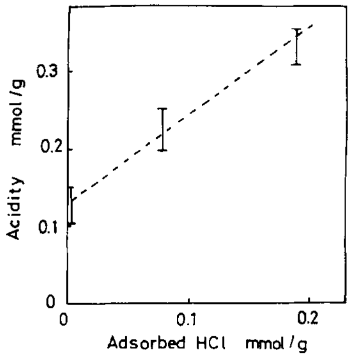

FIG. 4. Dependence of surface acidity on adsorption amounts of HCl.

larger than that of new OH groups of adsorbed HCl at 3400 cm^{-1}. The integrated intensity of the latter should be larger than that of the former. The relative extinction coefficient of the OH band of adsorbed water cannot be compared with that of other OH bands because it is not a single band. However, as shown in Fig. 3, the integrated intensity for one OH group in adsorbed HCl is larger than that of adsorbed water.

2. Surface Acidity of HCl–Alumina

A relationship between the adsorption amount of HCl on alumina and its surface acidity was obtained by using *n*-butylamine titration method. The results are shown in Fig. 4. The acidity of pure alumina evacuated at 500°C for 3 hr corresponded to 0.15 mmole/g, which is usually thought to be Lewis acidity. It was shown that the acidity of the HCl–alumina increased linearly with the adsorption amounts of HCl. Therefore, each adsorbed HCl could have created a new acid site in one to one correspondence in addition to acid sites originally present.

The *n*-butylamine titration method, however, gives only total acidity of the catalyst and we cannot obtain any information of the nature of acid sites. Therefore, the spectra of adsorbed pyridine on HCl–alumina were measured at room temperature. The catalyst, having maximum adsorption of HCl, was exposed to 7 mm Hg of pyridine for 15 min and subsequently evacuated for 1 hr at room temperature.

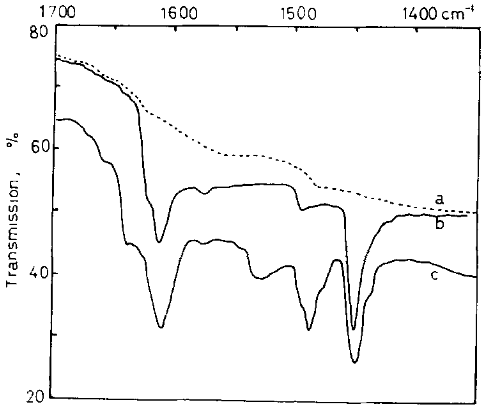

FIG. 5. Spectra of adsorbed pyridine: (a) alumina evacuated at 500°C; (b) pyridine adsorbed on alumina at 150°C; (c) pyridine adsorbed on HCl–alumina at room temperature [10 ml (STP) HCl/g was preadsorbed].

The absorption of bands of adsorbed pyridine were assigned to the bands observed by Parry (*1*) and Basila (*2*). The spectra obtained are given in Fig. 5. The band due to pyridinium ion is observed apparently at 1545 cm^{-1}, showing the existence of Brönsted acid sites. The ratio of Brönsted acid sites to Lewis acid sites was evaluated to be about 0.3 from the absorption intensity at 1545 cm^{-1} and 1450 cm^{-1} (Lewis acid) by the procedure described by Basila (*2*, *9*). If all of the adsorbed HCl formed Brönsted acid sites, it should be 3.2 ± 0.6.

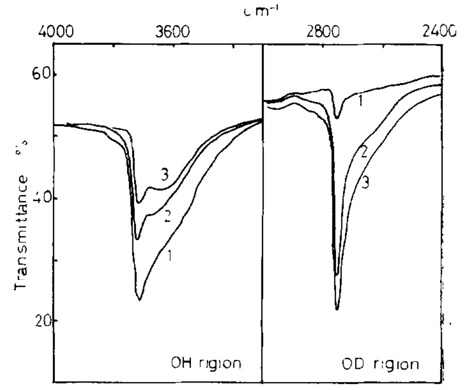

FIG. 6. Exchange of OH groups on silica surface with DCl in gas phase at room temperature: (1) partly deuterated silica evacuated at 500°C; (2) after exposure to 16 mm Hg of DCl; (3) after exposure to 27 mm Hg of DCl.

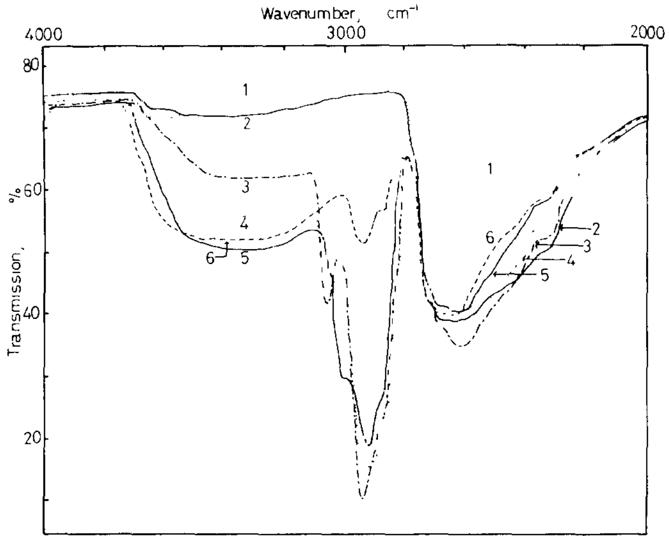

FIG. 7. Spectra during isomerization at room temperature: (1) deuterated alumina evacuated at 500°C; (2) DCl adsorbed on deuterated alumina; (3) 12 min after 20 mm Hg of 1-butene was admitted; (4) 63 min after 1-butene was admitted; (5) 16 hr after 1-butene was admitted; and (6) butene mixture was evacuated for a few minutes at room temperature after the reaction.

The difference thus suggests that a small fraction of new OH groups produced by adsorbed HCl had Brönsted acid character. Moreover, a new shoulder appeared in the band at 1450 cm^{-1} of HCl–alumina, which was not observed in the case of pure alumina. Therefore, it seemed that the properties of Lewis acid sites on HCl–alumina are different from those on pure alumina.

3. *Adsorption of DCl on Silica*

Figure 6 shows the treatment of silica with DCl evacuated at 500°C for 3 hr. The band at 3640 cm^{-1} is supposed to be assigned to the internal OH groups. When the silica disk was exposed to DCl, the intensity of these OH bands decreased and the new band due to OD band at 2740 cm^{-1} increased. Since deuterated silica showed the OD band at 2740 cm^{-1}, it is supposed that the surface OH groups converted to OD groups by exchanging OH groups with DCl. Nevertheless, DCl was scarcely adsorbed on silica and the band due to adsorbed DCl did not appear. The rate of exchange was very rapid and equilibrated in a few minutes. The exchange on the internal OH groups with DCl were very slow, as shown in Fig. 6.

4. *Infrared Spectra during the Course of Isomerization of 1-Butene*

The adsorption of DCl on the deuterated alumina was followed by admission of 1-butene at room temperature, and the infrared spectra were recorded at intervals. Typical results are shown in Fig. 7 and especially, the spectrum of adsorbed DCl on deuterated alumina is shown in Fig. 7 (2). In the 2790–2300 cm^{-1} region, two bands were observed; one is assigned to isolated OD groups centered at 2700 cm^{-1} and the other is due to hydrogen bonded OD groups produced by adsorbed DCl centered at 2480 cm^{-1}. Both bands were observed in overlapping. After 1-butene was introduced in a fixed amount, new bands appeared at 3400 cm^{-1}. These are attributed to hydrogen bonded OH groups and, at 2900 cm^{-1}, for butenes, as shown in Fig. 7 (3). After 16 hr from the beginning of the isomerization, butenes in the gas phase were evacuated at room temperature and intensities of the bands at 2700 and 2480 cm^{-1}, respectively, were compared with those before the reaction. The results are shown in Fig. 8. The intensities of the bands at 2480 cm^{-1} decreased more rapidly than the bands at 2700 cm^{-1} during the reaction. In this re-

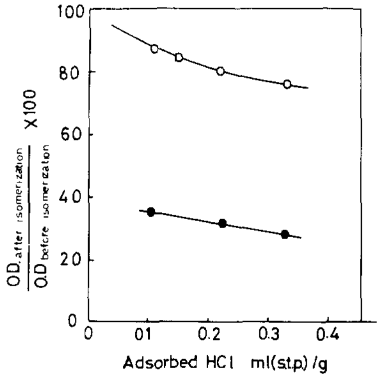

FIG. 8. Remaining fraction of each kind of OD groups after the isomerization: ○, isolated OH band at 2700 cm^{-1}; ●, new OH band produced by adsorbed HCl at 2480 cm^{-1}.

action system, the source of hydrogen was only in butenes. Consequently, it seems that the exchange of hydrogen between surface OD groups and butenes occurred because the intensity of two kinds of OD bands reduced in parallel with the growth of the intensity in the OH region. Thus, the rate of exchange can be expressed by using the rate of appearance of the new OH band, that is, the time dependence of the peak absorbance at 3400 cm^{-1}. The results are shown in Fig. 9. The optical density of OH bands at 3400 cm^{-1} during isomerization was plotted as a function of reaction time in this Fig. 9. It was found that the rate of exchange obeyed the following Elovich equation,

$$\text{rate} = be^{-\alpha D_{\mathrm{OH}}} \quad (1)$$

where b and α are constants and D_{OH} is the absorbance of the OH band appearing during isomerization. The rate of isomerization measured concurrently with the spectral observation did not obey the first order rate law, but applied to the Elovich equation as given in another report in detail (*10*). The initial rates of isomerization and the exchange reaction are presented in Table 1. It was found that both rates increased almost linearly with the adsorption amounts of DCl on the range of 0.1–0.3 ml (STP). Accordingly, the rates of isomerization were approximately proportional to that of the exchange. These results suggest that the OD groups from adsorbed DCl were more active, probably protonic, than isolated OD groups and the exchange process with butenes was involved in the course of isomerization.

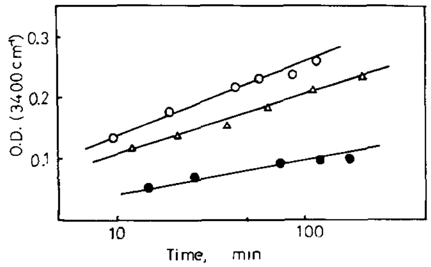

FIG. 9. Increase of OH band at 3400 cm^{-1} during isomerization: amount (ml; STP) of DCl on alumina: ○, 0.33; △, 0.22; and ●, 0.11.

In the case of silica, the equal molar mixture of DCl and 1-butene were similarly admitted into the cell after the pretreatment and the deuteration with DCl. Neither the exchange of OD groups to form OH groups nor the isomerization were observed up to 70°C. Accordingly, it was deduced that the exchange of DCl with 1-butene did not occur on silica surface.

DISCUSSION

It was found that the adsorption of HCl produces Brönsted acid sites on alumina besides Lewis acid sites originally present. Figures 4 and 5 show that the Brönsted acidity is attributed to the new OH groups produced by the adsorbed HCl.

The fact that the relative extinction coefficient of this new OH band was larger than that of any other OH bands implies that the

TABLE 1
INITIAL RATES OF ISOMERIZATION AND OD GROUPS EXCHANGE IN INFRARED CELL[a]

Adsorption amount of HCl (ml; STP)	Initial rate of isomerization (mm Hg/min)	Initial rate of exchange[b]
0.11	0.01	0.008
0.22	0.059	0.044
0.33	0.068	0.064

[a] 0.1 g of alumina disk, deuterated, room temperature, 20 mm Hg of 1-butene.

[b] Initial rates of exchange were obtained from the data in Fig. 9.

OH bonds made from adsorbed HCl are more ionic than that of other OH groups. Such a characteristic of the OH bond may be commonly observed on heterolytic dissociative adsorption, i.e., the heterolytic dissociation of HCl is formulated as $HCl + 2s \rightarrow \underset{s}{\underset{|}{H^{\delta+}}}\cdots\underset{s}{\underset{|}{Cl^{\delta-}}}$, where s is adsorption site, and $\underset{s}{\underset{|}{H^{\delta+}}}$ is more acidic than homolytic dissociation, $\underset{s}{\underset{|}{H}}$. Accordingly, the OH groups are supposed to form a coulombic hydrogen bond with adjacent $Cl^{\delta-}$, as proposed by Peri (*7*).

It was found by Noto and co-workers (*11*) that formic acid and acetic acid dissociatively adsorbed on alumina to produce the new OH groups. They suggested that the decomposition of formic acid on alumina was promoted by the proton from adsorbed formic acid or acetic acid. These results also support our consideration that Brönsted acid molecules are adsorbed dissociatively to produce acidic OH groups on alumina surface.

It was found from the infrared studies during isomerization that the acidic OH groups on HCl–alumina catalyzed the isomerization by transferring a proton between butenes and OH groups. Figure 8 indicates that acidic OH groups involved some fraction of isolated OH groups. This fact probably resulted from the OH bonds of some fraction of isolated OH groups becoming ionic by the inductive effect of adjacent Cl ion through the Al–O linkage as proposed by Chapman and Hair (*12*) in the case of fluorided silica.

The catalytic activity of HCl–alumina decreased during the isomerization and larger amounts of irreversible adsorption of butenes than pure alumina were observed. Polymerization may have occurred simultaneously with isomerization. In this connection, infrared spectra of adsorbed butenes in Fig. 7(6) show the polymeric product rather than olefin, because the absorption band due to the vinyl group disappeared.

Phenomena observed in the case of formic acid on silica (*11*) by Noto and coworkers were essentially the same as our result for HCl-treated silica. The adsorption amount of formic acid was less than 1/50 on alumina, and it adsorbed molecularly. The surface OH groups did not exchange with the adsorbed formic acid, but did exchange with gaseous acid. They concluded that the OH groups on silica surface catalyzed the decomposition of formic acid as protons.

From these results, it can be concluded that Brönsted acid molecules do not dissociate on silica surface and OH groups of silica are more polar than that of alumina. Kinetic results of the isomerization on HCl–alumina and the results of tracer studies on the deuterated catalysts are reported in the following paper (*10*).

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