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Infrared Spectroscopy of $C^{18}O_2$ on Alumina[1]

In spite of numerous infrared spectroscopy investigations of carbon dioxide chemisorbed on oxide surface, the nature of the adsorbed species is still an object of controversy (*1*). For example, three major bands (1652, 1460, and 1234 cm^{-1}) appearing below 1700 cm^{-1} in the infrared spectra of carbon dioxide chemisorbed on alumina were assigned to free and bidentate carbonate ions by Gregg and Ramsay (*2*), while Parkyns (*3*), using deuterated alumina and $C^{18}O_2$, assigned them to bicarbonate ion. Recently, Peri (*4*) reported the results of oxygen exchange between $C^{18}O_2$ and oxide catalysts including alumina, but lower frequency bands were not explored extensively. While we were investigating similar exchange reaction mainly by mass spectroscopy, we also carried out the infrared spectroscopy of $C^{18}O_2$ on alumina. In view of the background described above, it was thought to be useful to report the results obtained, those for lower frequency region in particular.

The catalyst used in this study was an η-alumina whose impurity level was below 0.02%. Fine powder of the alumina was pressed into a wafer of 19 mm diameter with a density of 17.8 mg/cm^2. The apparatus including cell was all glass with metal valves and a capacitance pressure transducer, and a routine pressure of 10^{-8} Torr (1 Torr = 133.3 N m^{-2}) range was obtained. The catalyst was calcined with dry air in the cell for 1 hr at 600°C followed by evacuation at the same temperature for 3 hr. When necessary, the catalyst was treated with deuterium at 600°C to convert hydroxyl groups to deuteroxyl groups. The original and deuterated surfaces are designated as H– and D–Al_2O_3, respectively. The BET surface area by nitrogen after the above treatment was 258 m^2/g. The isotopic purity of $C^{18}O_2$ used was 95.1 atom%.

Spectra were recorded with a Beckman IR4230 filter/grating spectrophotometer at a spectral slit width of 4 cm^{-1}. Usually the spectrum was recorded at a scanning speed of 50 or 20 cm^{-1}/min, but for frequency measurement it was recorded at 5 cm^{-1}/min with a polystyrene spectrum overlapped for calibration. Some typical spectra obtained with $C^{16}O_2$/H–, D–Al_2O_3, and $C^{18}O_2$/D–Al_2O_3 are shown in Fig. 1. It was found that some hydroxyl groups still remained after the deuteration, although quantitative evaluation was impossible because of a poor transmission in the 4000–3000 cm^{-1} region. Therefore, some bands on D–Al_2O_3 resulted from OH groups (marked with asterisk), which, however, rather helped to obtain the frequency shift by oxygen substitution on H–Al_2O_3. The frequency of bands observed and the shift caused by isotopic substitution are listed in Table 1. Besides the bands listed in Table 1, physically adsorbed carbon dioxide gave a band at 2362 cm^{-1} on H– and D–Al_2O_3, and partially exchanged $C^{18}O_2$ gave a couple of bands between 2330 and 2371 cm^{-1} in good agreement with the results of Peri (*4*).

The bands at 1900–1750 cm^{-1} and at 1180 cm^{-1} for $C^{16}O_2$ did not shift by the deuteration of catalyst, but they did shift by oxygen exchange as is clear in Fig. 1.

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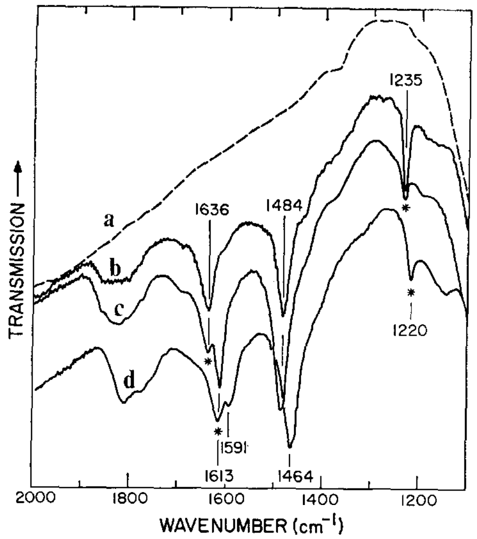

FIG. 1. Infrared spectra of carbon dioxide on alumina. (a) Alumina; (b) $C^{16}O_2$ (0.1 Torr) on $H\text{–}Al_2O_3$; (c) $C^{16}O_2$ (3 Torr) on $D\text{–}Al_2O_3$; (d) $C^{18}O_2$ (2.5 Torr) on $D\text{–}Al_2O_3$ (^{18}O = 90.5%). (*) Bands resulted from residual OH groups. Spectrum (d) is displaced vertically for clarity.

The shift was 20–30 cm^{-1} for all bands, although it was difficult to measure accurately because the bands were broad and overlapping. In agreement with the previous investigators (*3*, *4*), these bands are probably due to a bidentate or bridged carbonate. No shift by deuteration and a shift by oxygen exchange support this assignment. These bands were easily removed by pumping at room temperature.

The mass spectrometric study showed that the oxygen exchange readily occurred on adsorption as Peri (*4*) observed. On the present alumina, it occurred even at room temperature to some extent. Therefore, the gas was condensed and evaporated back repeatedly during the adsorption and the gas finally evaporated was analyzed by a mass spectrometer attached to the apparatus. It is of interest that some bands shifted as a function of the ^{18}O concentration in the progress of exchange reaction (between spectra c and d in Fig. 1), while the shift of other bands occurred in different manners. Figure 2 illustrates these findings. A deuteroxyl band at medium frequency (2756 cm^{-1}) did not shift at adsorption temperatures up to 180°C, but when $C^{18}O_2$ was adsorbed at 475°C, it shifted to 2737 cm^{-1} and remained unchanged after that (Fig. 2a). The lowest frequency deuteroxyl band (2730 cm^{-1}) probably behaved similarly and finally shifted to 2710 cm^{-1}, but the detailed shift could not be followed because this band was on the shoulder of the central band. Deuteroxyl band at the highest frequency (2785 cm^{-1}) disappeared

TABLE 1

Infrared Bands on Isotopic Substitution

ir bands (cm^{-1})			$\Delta\nu$ by H with $C^{16}O_2$	$\Delta\nu$ by O on $D\text{–}Al_2O_3$	Assignment
$C^{16}O_2$ $H\text{–}Al_2O_3$	$C^{16}O_2$ $D\text{–}Al_2O_3$	$C^{18}O_2$ $D\text{–}Al_2O_3$			
3777	2785	2769[a]	992	16	ν_{OH} of catalyst
3740	2756	2737	984	19	
3705	2730	(2710)[b]	975	(20)[b]	
3614	2664	2646	950	18	ν_{OH} (HCO_3^-)
(1900–1750)[b]	(1900–1750)[b]	(1870–1720)[b]	(0)[b]	(20–30)[b]	Asym. ν_{CO} (bidentate or bridged CO_3)
1636	1613	1591	23	22	Asym. ν_{CO} (HCO_3^-)
1484	1485	1464	0	21	Sym. ν_{CO} (HCO_3^-)
1235	—	(1220)[c]	—	(16)[c]	C–O–H bend (HCO_3^-)
(1180)[b]	(1180)[b]	(1150)[b]	(0)[b]	(30)[b]	Sym. ν_{CO} (bidentate or bridged CO_3)

[a] Appeared after the removal of gas.

[b] Frequency with a larger error than others.

[c] Frequency and shift on $H\text{–}Al_2O_3$.

as soon as $C^{18}O_2$ was admitted even at room temperature, and two new bands appeared at 2664 and 2646 cm^{-1} (Fig. 2b). This is apparently due to the formation of bicarbonate ions ($D^{16}O{-}CO_2^-$ and $D^{18}O{-}CO_2^-$). The frequency shift between ^{16}OD and ^{18}OD calculated simply from the reduced masses is 16.3 cm^{-1} which is in good agreement with the observed split of 18 cm^{-1}. After an extensive exchange, only the 2646 cm^{-1} band remained, and, upon evacuation at elevated temperature, the deuteroxyl band reappeared at 2769 cm^{-1}.

In contrast to the bands discussed above, bands at 1613 and 1485 cm^{-1} shifted smoothly with the concentration of ^{18}O in the gas phase (Fig. 2c and d). Although complete isotopic equilibration between the gas and adsorbed phases could not be guaranteed, this result indicates that the oxygen atoms in those surface species were gradually replaced by heavy oxygen atom. The frequencies listed in the third column of Table 1 were obtained from the extrapolation of the curves in Fig. 2. Bands at 1636 and 1484 cm^{-1} together with those at 3614 and 1235 cm^{-1} ($C^{16}O_2$/H–Al_2O_3) are assigned to various modes of vibration of bicarbonate ion as listed in Table 1. The frequency of the asymmetric C–O stretching vibration is shifted by 23 cm^{-1} by deuteration. Bernitt *et al.* (*5*) also reported that the asymmetric ν_{CO} of bicarbonate ion shifted by 10 cm^{-1} by substituting D for H, while no shift was observed for the symmetric ν_{CO}. The present assignment is the same as that made by Parkyns (*3*), but he did not observe any shift for ν_{OH} of bicarbonate ion with $C^{18}O_2$. This led him to infer the breakage of Al–O bond of hydroxyl groups on alumina to form bicarbonate ion. Our results, however, showed that two kinds of bicarbonate species were formed as a result of adsorption and exchange. The amount of $C^{18}O_2$ used by Parkyns may have been too small compared to the amount of catalyst. Our results also show that the oxygen of alumina surface including hydroxyl groups at the highest frequency is exchanged readily with carbon dioxide probably through bicarbonate and/or bidentate carbonate ions even at room temperature, while the oxygen atoms of the other hydroxyl groups are exchanged only at high temperatures.

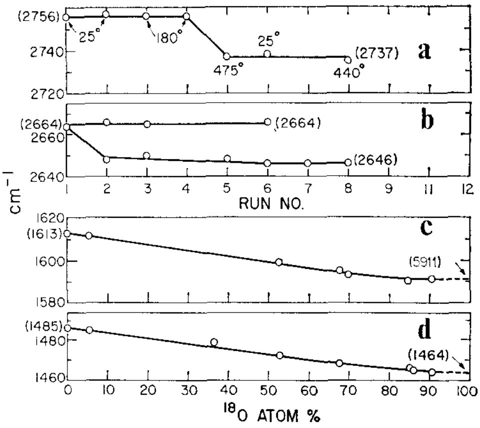

FIG. 2. Frequency shift as a function of run number (a and b) and of isotopic composition (c and d).

When $C^{16}O_2$ was adsorbed at 390°C on H–Al_2O_3 and removed at 265°C, the intensities of the 1636, 1484, and 1235 cm^{-1} bands were reduced to about one tenth of those in Fig. 1. At the same time, other bands at 1590, 1520, and 1440 cm^{-1} became clear as shoulders on the bicarbonate bands. Therefore, other surface species, perhaps unidentate and/or free carbonate, could also exist in much smaller quantities but in a more stable form.

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