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Infrared Study of Carbon Dioxide Adsorbed on Magnesium and Calcium Oxides

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The infrared absorption spectra of CO_2 adsorbed on MgO and CaO were measured in the wide region 700—4000 cm^{-1} at various amounts of adsorbed CO_2 and temperatures of adsorption and desorption. It has been found that both uni- and bidentate carbonates are formed on MgO when a small amount of CO_2 is adsorbed and that unidentate carbonates predominate as the amount of adsorbed CO_2 is increased. On the other hand, only unidentate species were formed on CaO at room temperature independently of the amount of adsorbed CO_2, but bidentate species were also formed on CaO when the temperature of adsorption was high. The unidentate carbonates formed on both MgO and CaO at room temperature partially changed to bidentate carbonates upon evacuation at higher temperatures. The correlation between $\Delta\nu=|\nu_1-\nu_5|$ and the partial charge on oxygen atoms of various oxides, which corresponds to basic strength on the surface, was examined.

Calcium and magnesium oxides were reported recently to catalyze the esterification of benzaldehyde,[1] the dehydrochlorination of chlorinated ethanes,[2] the decomposition of diacetone alcohol[3] and the isomerization of olefins such as 1-butene,[4] limonene *etc.*[5] It has been pointed out that their catalytic activities are entirely due to the surface basic properties[1-5] and depended largely on the amount of adsorbed carbon dioxide.[3,4] Therefore, it is desirable to study the adsorption of acidic carbon dioxide on the basic oxides in order to characterize the basic properties.

Infrared studies of adsorbed CO_2 have been made for various oxides such as NiO,[6] TiO_2,[7] ZnO,[8] BeO[9] and MgO[10,11] but not for CaO. As for MgO, the formation of bidentate carbonate and carbonate ion was reported by Gregg and Ramsay[10] and that of bi- and unidentate carbonates by Evans and Whateley.[11] However, since the former authors did not observe the spectra in the low frequency region below 1200 cm^{-1}, while the latter ones did not study the spectral change with the amount of adsorbed CO_2, we attempted to observe the spectra in the region of 4000—700 cm^{-1} by varying greatly the amounts of adsorbed CO_2 and by changing the temperature of desorption to make clearer the behavior of adsorbed species. The spectra of CO_2 adsorbed on CaO were observed similarly to those for MgO. It is the purpose of the present work to distinguish the difference in adsorbed species of CO_2 between MgO and CaO and to study the correlation of basic properties of the oxides with the observed spectral data.

Experimental

Thin discs of calcium hydroxide (guaranteed reagent of Kanto Chemical Co.) and basic magnesium carbonate (guaranteed reagent of E. Merck Co.) prepared by pressing at 120 kg/cm^2 were mounted on a Nichrome wire holder placed in the heating zone of an infrared cell and decomposed to their oxides by evacuating at 700 °C for 3 hr. The calcined discs were moved into the optical path with a magnet and evacuated to about 4×10^{-6} mmHg at room temperature. The cell (66.8 ml of a dead space) was constructed of quartz and had cemented sodium chloride windows.

The amounts of CO_2 (99.99% purity) dosed into the cell were determined volumetrically. The spectra of adsorbed CO_2 were observed 30 min after CO_2 was introduced. Since no absorption band for free CO_2 (2350 cm^{-1}) was observed in any experiment, all the CO_2 dosed were regarded as adsorbed on the oxides. Desorption of CO_2 was carried out by evacuating samples at temperatures of 25—700 °C for 30 min.

All the measurements of infrared spectra were carried out at room temperature with a Hitachi model 215 infrared spectrophotometer.

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[9] W. I. Stuart and T. L. Whateley, *Trans. Faraday Soc.*, **61**, 2763 (1965).

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[11] J. V. Evans and T. L. Whateley, *Trans. Faraday Soc.*, **63**, 2769 (1967).

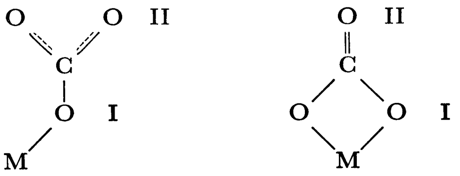
The weights of the samples determined after a series of IR spectral measurements were 10.0 and 20.8 mg for MgO in Fig. 1 and CaO in Fig. 3, respectively. The surface areas measured by nitrogen adsorption were 52 and 158 m^2/g, respectively, for CaO and MgO evacuated at 700 °C for 3 hr.

Results and Discussion

Both calcium and magnesium oxides heat-treated at 700 °C *in vacuo* for 3 hr showed infrared absorption bands at 840—1100 cm^{-1} (a broad band at 1000 cm^{-1} and a weak one at 840 cm^{-1} on MgO; a weak band at 1100 cm^{-1} and a broad one at 1060 cm^{-1} on CaO) which are due to the oxides themselves but no bands for OH and CO_2 which are possible impurities in the oxides. Both samples on which CO_2 was adsorbed showed no bands above 1700 cm^{-1}.

Adsorption of CO_2 on MgO at Room Temperature. Figure 1 shows the spectral changes caused by varying the amounts of CO_2 adsorbed on MgO. The stronger bands at 1670, 1315, 1000 and 850 cm^{-1} and the broad or weak bands at 1550, 1410 and 1050 cm^{-1} were observed in spectrum (2) of Fig. 1, where 0.23×10^{-3} mmol of CO_2 was adsorbed. In spectrum (3) of Fig. 1 where the adsorbed amount of CO_2 was increased, new bands appeared at 1630, 1280, 950 and 830 cm^{-1} and all the bands increased in intensity in spectrum (4). In spectra (5) and (6), the intensity of the bands at 1550, 1410, 1050 and 860 cm^{-1} increased, while the intensity of the other bands decreased.

On the basis of the analysis by Fujita *et al.*,[12] Evans and Whateley[11] considered that the splitting of the carbonate ion asymmetric stretching band (ν_3) is about 100 and 300 cm^{-1} for unidentate and bidentate carbonate, respectively, as shown below.[13] And they reported that the bands at 1665, 1325, 1005 and 850 cm^{-1} observed for CO_2 adsorbed on MgO could be assigned



unidentate complex bidentate complex

to the bidentate carbonate complex and those at 1510, 1390, 1035 and 865 cm^{-1} to the unidentate carbonate complex. They attributed the strong bands at 1625 and 1275 cm^{-1} to bidentate carbonate or bridging carbonate because of the large splitting of the two bands. However, if bridging carbonate is of the type $\genfrac{}{}{0pt}{}{-O}{-O}\!\!>C{=}O$, the band should appear at 1750 cm^{-1}.[14] Therefore, the bands at 1625 and 1275 cm^{-1} are believed due to bidentate carbonate. From these results, the bands at 1670, 1315, 1000 and 850 cm^{-1} and those at 1630, 1280, 950 and 830 cm^{-1} are assigned to bidentate carbonate. The bands at 1550, 1410, 1050 and 860 cm^{-1} can be assigned to the unidentate carbonate complex.

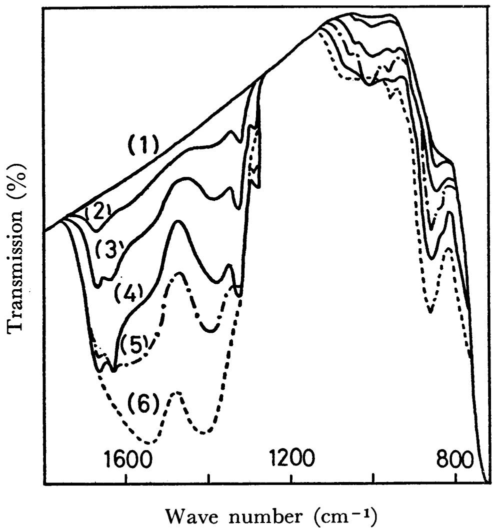


Fig. 1. Spectral changes for CO_2 adsorbed on MgO at room temperature for various adsorbed amounts; (1); 0 mmol (background), (2); 0.23×10^{-3} mmol ($\theta=0.02$), (3); 0.69×10^{-3} mmol ($\theta=0.06$), (4); 2.2×10^{-3} mmol ($\theta=0.16$), (5); 2.9×10^{-3} mmol ($\theta=0.25$), (6); 5.2×10^{-3} mmol ($\theta=0.38$).

It is concluded from these observations that both uni- and bidentate carbonates are formed on MgO when a small amount of CO_2 is adsorbed and that unidentate carbonate is predominantly formed when there is a large amount of adsorbed CO_2.

Desorption of CO_2 from MgO. The changes in the spectra of a sample, which had CO_2 adsorbed at room temperature, produced by evacuation at 25—700 °C for 30 min are shown in Fig. 2. In spectra (1)

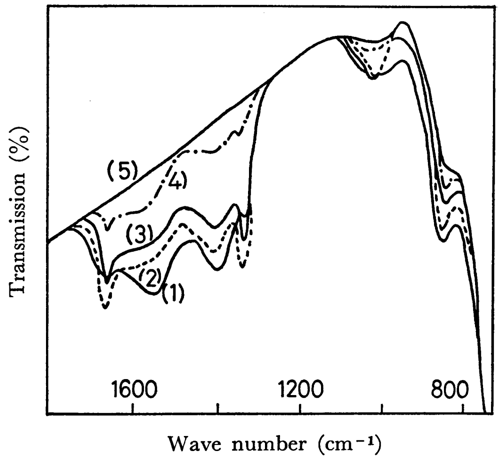


Fig. 2. Spectral changes due to CO_2 desorption from MgO at various evacuation temperatures; (1); room temp, (2); 240 °C; (3); 300 °C; (4); 400 °C (5); 700 °C.

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[12] J. Fujita, A. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).

[13] Evans and Whateley[11] assumed that $\Delta\nu=|\nu_1-\nu_5|$ is a splitting of the carbonate ion asymmetric stretching band (ν_3), where ν_1 represents $\nu(\mathrm{C-O_{II}})+\nu(\mathrm{C-O_I})$, $\nu(\mathrm{C-O_{II}})$ and ν_5 does $\nu(\mathrm{C-O_{II}})$, $\nu(\mathrm{C-O_I})+\delta(\mathrm{O_ICO_{II}})$ for uni- and bidentate carbonate complexes, respectively.[12] However, Fujita *et al.*[12] say that it is impossible to determine which of three C–O stretching vibrations is due to the splitting of ν_3. Therefore, $\Delta\nu$ was used instead of the splitting of ν_3 in the present work.

[14] L. H. Little, "Infra-Red Spectra of Adsorbed Species," Academic Press, London and New York (1965).

where the sample was evacuated at room temperature, broad bands appeared at 1550, 1410 and 1050—1000 cm^{-1} with weak bands at 1670, 1330 (shoulder) and 845 cm^{-1}. These bands were not changed by evacuation at 100 °C. By elevating evacuation temperature to 240 °C (spectra (2)), the spectra were changed greatly. The bands at 1550 and 1410 cm^{-1} decreased in intensity, while those at 1670 and 1330 cm^{-1} increased. The bands at 1050—1000 cm^{-1} became sharp at 1030 cm^{-1} and the band at 845 cm^{-1} shifted to 855 cm^{-1}. All bands decreased greatly in intensity on evacuation at 400 °C and the bands at 1800—1100 cm^{-1} disappeared at 700 °C.

The spectral changes caused by CO_2 desorption indicate that some unidentate carbonate is converted to bidentate carbonate by evacuation at 240 °C and both carbonates disappear at 700 °C.

Adsorption of CO_2 on CaO at Room Temperature. The absorption spectra of CO_2 adsorbed on CaO are shown in Fig. 3. Five bands were observed at 1520, 1490, 1415, 1060 and 860 cm^{-1} when 2.8×10^{-4} mmol of CO_2 was adsorbed. With an increase in the amount of adsorbed CO_2, the intensities of these bands increased and those at 1520 and 1490 cm^{-1} became a broad band at 1510 cm^{-1}. When the amount of adsorbed CO_2 was increased to more than 8.2×10^{-3} mmol, a band appeared at 2350 cm^{-1} and it disappeared upon evacuation at room temperature. Since the band at 2350 cm^{-1} is assigned to gaseous CO_2 and 8.2×10^{-3} mmol of dosed CO_2 corresponds to $\theta=0.96$ (calculated by assuming that the cross-section area of CO_2 is 19.5 Å^2), the five bands are attributed to the surface species. Because the value of $\Delta\nu$ is about 100 cm^{-1}, these bands may be assigned to a unidentate carbonate complex and the bands at 1520—1490, 1415, 1060 and 860 cm^{-1} to $\nu(\text{C–O}_{\text{II}})$, $\nu(\text{C–O}_{\text{II}})+\nu(\text{C–O}_{\text{I}})$, $\nu(\text{C–O}_{\text{I}})+\nu(\text{C–O}_{\text{II}})$ and π vibrations, respectively. Thus, the adsorbed species of CO_2 on CaO is different from that on MgO and only unidentate carbonate independent of the amount of adsorbed CO_2 is formed.

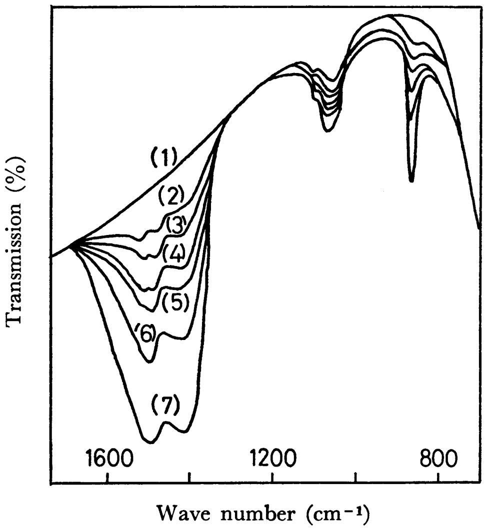

Fig. 3. Spectral changes for CO_2 adsorbed on CaO at room temperature at various adsorbed amounts; (1); 0 mmol (background) (2); 2.8×10^{-4} mmol ($\theta=0.03$), (3); 5.6×10^{-4} mmol ($\theta=0.06$), (4); 9.3×10^{-4} mmol ($\theta=0.10$), (5); 1.2×10^{-3} mmol ($\theta=0.13$), (6); 2.4×10^{-3} mmol ($\theta=0.26$), (7); 5.0×10^{-3} mmol ($\theta=0.55$).

Desorption of CO_2 from CaO. The spectral changes produced by CO_2 adsorbed on CaO at room temperature and evacuated at 310—700 °C are shown in Table 1. Many bands were observed when the sample was evacuated at 210—370 °C and new bands appeared upon evacuation at 110 and 210 °C.

On the basis of the observed characteristic features of the spectral changes upon CO_2 desorption, the bands other than unidentate species bands are classified into the following two groups; one (B_1) include bands at 1635, 1290—1302 and 980 cm^{-1} and the other (B_2) include bands at 1550—1570, 1308—1315, 1050 and 850 cm^{-1}. Since the value of $\Delta\nu$ is about 300 cm^{-1} in both the groups, they are assigned as bidentate carbonate complexes.

The behavior of CO_2 adsorbed on CaO is shown below,

$$\begin{tikzcd}
 & CO_2\ (g) & \\
B_1 \arrow[d, "370\text{—}440\ ^\circ C"] & U \arrow[l, "210\text{—}370\ ^\circ C"'] \arrow[u, "\text{above } 110\ ^\circ C"'] \arrow[r, "\text{above } 110\ ^\circ C"'] & B_2 \arrow[d, "\text{above } 370\ ^\circ C"] \\
CO_2\ (g) & & CO_2\ (g)
\end{tikzcd}$$

where U is the unidentate carbonate complex.

Table 1. Changes of the bands upon evacuation at various temperatures

Evac. temp. °C	25	110	210	310	370	460
		B_2 1570(A) 1308(A)	B_2 1570(I) 1308(I)	B_2 1550(I) 1315	B_2 1550(D) 1315(D)	B_2 1550 1315 1050 850
			B_1 1635(A) 1290(A) 970(A)	B_1 1635(I) 1302 980	B_1 1635(D) 1302(D) 980(D)	
	U 1500 1420 1060 860	U 1500(D) 1420(D) 1060 860	U 1500(D) 1420(D) 1060 860	U 1500(D) 1420(D) 1050 850	U 1500(D) 1420(D) 1050(D) 850(D)	

U: Unidentate carbonate, B_1, B_2; Bidentate carbonate, (I); Increase in intensity of the band, (D); Decrease in intensity of the band, (A); New band appeared by evacuation.

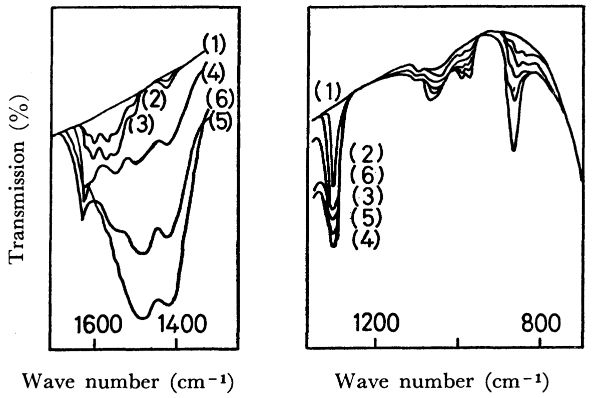

Fig. 4. Spectral changes for CO_2 adsorbed on CaO at 350 °C for various adsorbed amount; (1); 0 mmol (background), (2); 0.23×10^{-3} mmol, (3); 0.46×10^{-3} mmol, (4); 0.69×10^{-3} mmol, (5); 2.2×10^{-3} mmol, (6); 2.5×10^{-3} mmol.

Adsorption of CO_2 on CaO at 350 °C. Figure 4 shows the spectral changes produced by varying the amount of CO_2 which was adsorbed on CaO at 350 °C.

In the case of a small amount of adsorbed CO_2, the bands at 1635—1550 and 1308—1302 cm^{-1} were stronger than those around 1500 and 1430 cm^{-1} and the latter increased with increasing amount of adsorbed CO_2. Judging from the value of $\Delta\nu$, the former bands can be assigned to a bidentate carbonate complex and the latter to a unidentate carbonate complex, though it is difficult to assign all bands observed.

Correlation of $\Delta\nu=|\nu_1-\nu_5|$ with the Partial Charge δ_0 on Oxygen of Metal Oxides. It was reported that the active sites of MgO and CaO for decomposition of diacetone alcohol are basic sites (O^{2-} ions) and the activity is related to the partial charge on oxygen or the basic strength of the oxides.[15] Since CO_2 is bonded to surface oxygen to form uni- or bidentate carbonates, $\Delta\nu$ is also expected to be related to δ_0. In the case of bidentate carbonate, the values of $\Delta\nu$ are known to be 420 cm^{-1} for BeO[9] and were found to be 350 and 240 cm^{-1} for MgO and CaO, respectively. The values of δ_0 for BeO, MgO and CaO are known to be -0.35, -0.50 and -0.57 respectively.[16] Therefore, a correlation between $\Delta\nu$ and δ_0 seems to exist in the case of alkaline earth metal oxides. However, the correlation does not hold in the cases of TiO_2[7] and ThO_2.[17] This seems to indicate that the magnitude of $\Delta\nu$ does not depend only on δ_0, since CO_2 needs to bond not only to surface oxygen, but also to surface metal for the formation of bidentate carbonate.

In the case of unidentate carbonate, the values of $\Delta\nu$ are known to be 150—190 cm^{-1} for ZnO[8], TiO_2[7] and ThO_2[17] and were found to be 140 and 70 cm^{-1} for MgO and CaO respectively. Since δ_0 values for these oxides are $-0.27\sim-0.29$, -0.50 and -0.57 respectively, there exists a fairly good correlation. However, more data for $\Delta\nu$ with oxides will be needed for a full discussion of this correlation.

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16) R. T. Sanderson, *Inorg. Chem.*, **3**, 925 (1964).

17) P. Pichat, J. Véron, B. Claudel, and M. V. Mathieu, *J. Chim. Phys.*, **63**, 1026 (1966).