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Transient Analysis of IR Transmission Spectroscopy by Using a Spectroscopic Flow Reactor for In Situ Studies of Heterogeneous Catalysis*

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Abstract

A spectroscopic flow reactor was developed to study in situ conditions of heterogeneous catalysis which was in a transient state in various reaction gas compositions at a temperature range of 280~800°C. The reactor showed the transient behavior of adsorption and desorption of CO and CO_2 on magnesium oxide which was predehydrated at 350 (S_{350}) and 800°C (S_{800}). The detailed analysis of the adsorption bands obtained demonstrated extraordinary differences in their transient behavior between S_{350} and S_{800}, and made it possible to assign many kinds of species, which were derived from the interaction of surface sites with adsorbates especially the hydroxyls, on local surface sites.

1. Introduction

In situ investigations of heterogeneously catalysed reactions have been extensively developed by using a large variety of spectroscopic techniques resulting from the recent rapid progress of surface analysis procedures[1]. One valuable technique is infrared transmission spectroscopy and, generally speaking, the spectroscopic analysis of a thin disk of the samples in continuous or occasional contact with various gases in a closed system. The closed system has some disadvantages such as (1) always having unsteady stste conditions under measurements up to the point of an equilibrium condition, (2) difficulty in detecting unstable intermediates formed in the course of reactions because of their small amounts and unstable species, and (3) unexpected effects of products on adsorbed species.

In the present study, our interests are concentrated on the two purposes as shown in the following. The first is the development of a spectroscopic flow reactor for in situ studies of heterogeneous catalysis under transient conditions. The flow reactor has the advantage of detecting unstable species during reactions, because greater amounts of the species should be formed under the reaction steady states in the flow system than under the closed system, according to the

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value of rate constants for their decomposition. The intermediates are thus accumulated on the surface when their decomposition is one of the rate controlling steps.

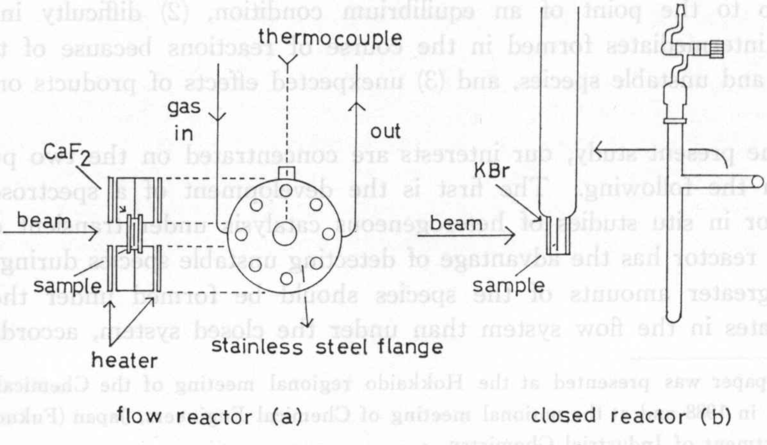
The second purpose is to study the transient state of surface species by using the spectroscopic flow reactor. As has been demonstrated so far by a large number of investigators,[2)] magnesium oxide is one of the most valuable catalysts for spectroscopic study and it is easy to analyse the spectroscopic bands. Carbon monoxide and carbon dioxide were chosen as the adsorbates since CO and CO_2 form a variety of adsorbed species and interact with each other depending on coexisting surface species, especially surface hydroxyls. The composition and temperature of the reaction gas were changed stepwisely and linearly elevated, respectively.

2. Experimental Method

(1) Description of the Reaction Systems

Fig. 1 (a) illustrates the details of the spectroscopic flow reactor. The reactor was developed by referring to Penninger's[3)] and Bell's[4)] IR cells. The reactor was made of stainless steel flanges. In each half of the reactor body, calcium fluoride windows (2 cm in diameter and 0.3 cm in thickness) were mounted and sealed with teflon gaskets, and an infrared beam was able to be passed the windows and reach the detector of the spectrometer during the reaction. The two halves of the reactor were sealed by a copper gasket. The catalyst of 20 mg was compressed by 120 kg/cm^2 to make a thin disk of 20 mm diameter, and which was held in the reactor. The assembled reactor had a dead volume of only 0.77 cm^3. The reactor was heated by 100 watt disk heaters, and the catalyst temperature was measured by a sheathed thermocouple of Kc (alumel chromel) of 1 mm diameter, which was inserted in the port of the reactor body.

The reactor was connected to the flow controlling system which could prepare



flow reactor (a)　　closed reactor (b)

Fig. 1. Schematic drawing of the in situ IR flow reactor (a) and closed reactor (b).

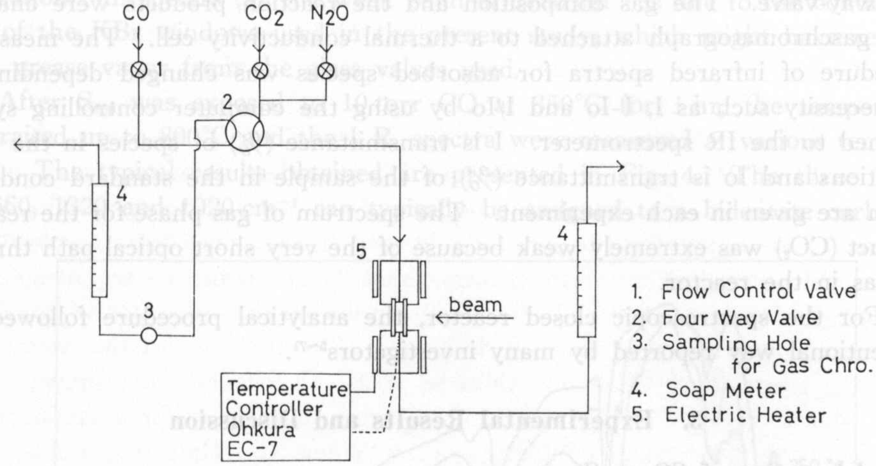


Fig. 2. Schematic drawing for experimental apparatus.

three gas feeds with different gas compositions at the same total gas flow rate. The dead time of the system was about 30 sec at most, using a total gas flow rate of 40 ml/min. Fig. 2 illustrates the schematic drawing of the experimental apparatus for the flow controlling system. The four-port valve was set to change the gas composition without change in the total flow rate of feed gases. When it was necessary to use the system to analyse the resulting species accurately without any water vapor and impurities, the standard cylinder gases which were used had a purity of 99.5% CO, 99.99% CO_2 and 99.9% N_2O. In addition, a closed IR cell was also used to take reference spectra for the various samples under the standard conditions. Fig. 1 (b) is the scheme of the closed IR cell.

Transmission infrared spectra of the species adsorbed on MgO were obtained with a Hitachi 260-50 infrared spectrometer assisted by a computer controlling system, using resolution of 1.5 cm^{-1}.

(2) Materials

Magnesia was obtained from both Wako Co. and Merck. The B. E. T. surface areas were 28 for S_{350} from Wako, 54 for S_{350} and 25 m^2/g for S_{800}, both from Merck. Carbon monoxide (99.5% CO) and Carbon dioxide (99.99% CO_2) were obtained from Takachiho Co. and not further purified. D_2O (99.75% D_2O) was supplied from Wako Co.

The different samples of MgO (Wako and Merck) were prepared by dehydrating them at 350 and 800°C in vacuum conditions for 3 hrs and designating the surfaces as S_{350} and S_{800}. It has been confirmed that no appreciable differences are detected between Merck and Wako's samples for the adsorbed species.

(3) Procedure

For the spectroscopic flow reactor, the temperature of the catalyst was raised in a pure He stream which was then switched over stepwisely to a gas stream containing adsorbates with no change in total gas flow rate by using a four way-valve. The gas composition and the reaction products were analysed by a gaschromatograph attached to a thermal conductivity cell. The measuring procedure of infrared spectra for adsorbed species was changed depending on the necessity such as I, I-Io and I/Io by using the computer controlling system attached to the IR spectrometer. I is transmittance (%) of species in the given conditions and Io is transmittance (%) of the sample in the standard conditions which are given in each experiment. The spectrum of gas phase for the reaction product (CO_2) was extremely weak because of the very short optical path through He gas in the reactor.

For the spectroscopic closed reactor, the analytical procedure followed the conventional way reported by many investigators[5~7].

3. Experimental Results and Discussion

3-1. Adsorption of CO on S_{800}.

Fig. 3 illustrates the backgrounds of IR spectra for various samples of MgO. The spectrum (a) is for a clean surface obtained by heating the sample at 800°C for 3 hrs under lower than 10^{-3} torr, indicating much less amounts of OH and carbonate groups. The spectra of (b), (c), and (d) are for S_{350}, S_{800} which were exposed to various gases successively, in the order of H_2O 10 torr→CO_2 10 torr→evacuation, and $MgCO_3$, respectively. Comparing the four spectra, one may recognize the existence of two different carbonate species on the surface, or bulk magnesia such as bridged and unidentate, which has been demonstrated by a large number of investigators[5~7]. In addition, the band at 3750 cm^{-1} clearly shows the residual free OH commonly existing on each surface, even at 350°C

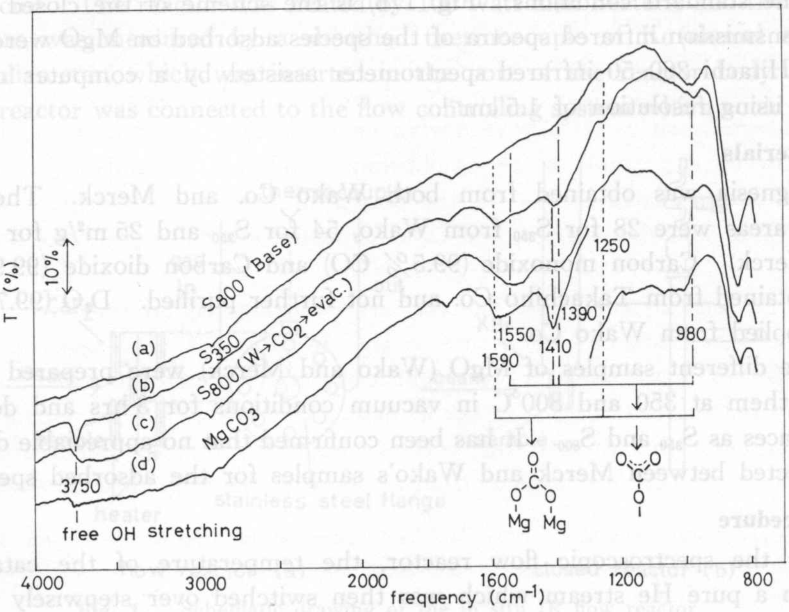


Fig. 3. IR spectra of the background of MgO dehydrated at various conditions.

evacuation. In spectra (a), the weak band at 1730 cm^{-1} is due to the contamination of the KBr windows used in the present study, which might have resulted from grease vapor from the glass valves used.

After S_{800} was exposed to 10 torr CO at 350°C for 1 hr, the temperature was raised up to 800°C and the I. R. spectra were measured at various temperatures. The typical results obtained are presented in Fig. 4. The three bands at 1660, 1320 and 1020 cm^{-1} can typically be assigned to a bidentate carbonate

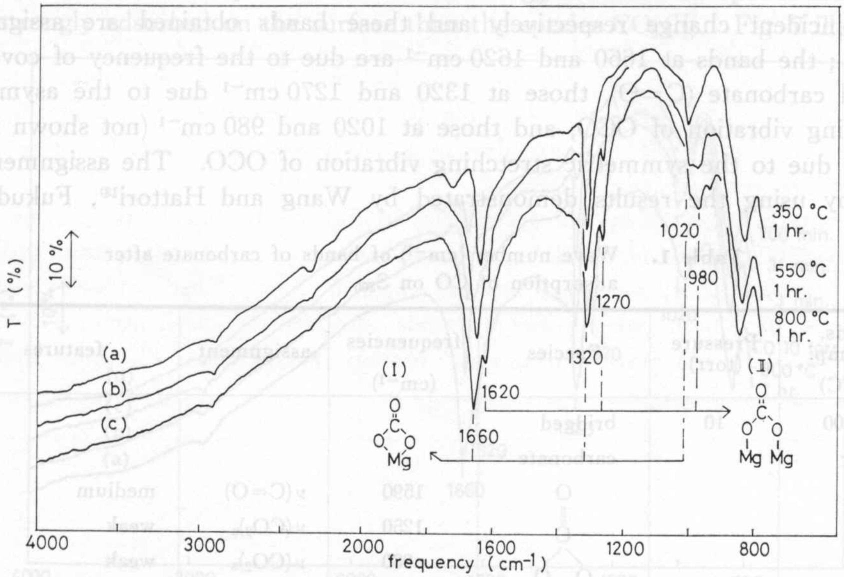


Fig. 4. IR spectra of CO adsorbed on S_{800} at increasing temperatures from 350 to 800°C.

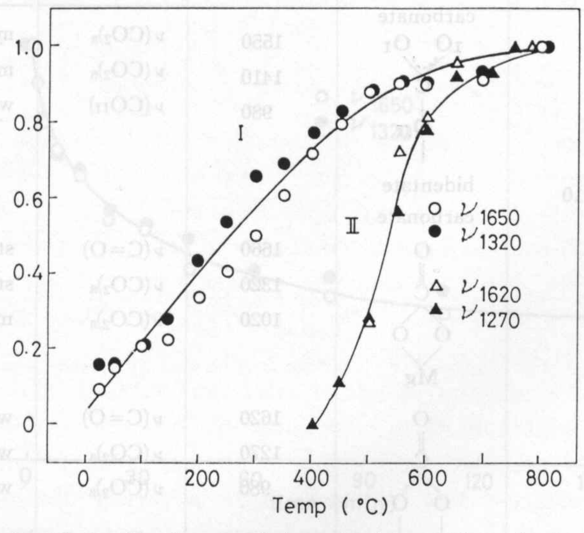
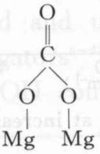
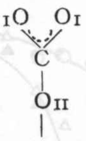
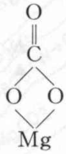
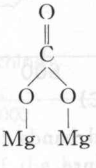


Fig. 5. Intensity change of the paired bands for adsorbed CO on S_{800} at rising temperature.

species (I) whose intensity grows with increasing temperature. New bands at 1620, 1270, and 980 cm^{-1} appear at temperatures higher than 500°C, which might be attributed to bridged carbonate (II), taking into account a large amount of excellent work by Zecchina's school[8~12)].

Fig. 5 illustrates the relative intensity change (I/Io) of two paired bands at 1650～1320 {CO_3 (I)} and 1620～1270 {CO_3 (II)} cm^{-1} depending on the adsorption temperature. Here, Io is the transmittance of the band which gives the lowest peak, and I is that under the given conditions. Each paired band clearly shows the coincident change respectively and these bands obtained are assigned as follows; the bands at 1660 and 1620 cm^{-1} are due to the frequency of covalently bonded carbonate (C=O), those at 1320 and 1270 cm^{-1} due to the asymmetric stretching vibration of OCO, and those at 1020 and 980 cm^{-1} (not shown in this figure), due to the symmetric stretching vibration of OCO. The assignment was done by using the results demonstrated by Wang and Hattori[13)], Fukuda and

Table 1. Wave number (cm^{-1}) of bands of carbonate after adsorption of CO on S_{800}

Ads. temp. (°C)	Pressure (torr)	Species	frequencies (cm^{-1})	assignment	features
300	10	bridged carbonate 	1590 1250 980	ν(C=O) $\nu(CO_2)_a$ $\nu(CO_2)_s$	medium weak weak
800	10	unidentate carbonate 	1550 1410 980	$\nu(CO_2)_a$ $\nu(CO_2)_s$ $\nu(CO_{II})$	medium medium weak
		bidentate carbonate 	1660 1320 1020	ν(C=O) $\nu(CO_2)_a$ $\nu(CO_2)_s$	strong strong medium
			1620 1270 980	ν(C=O) $\nu(CO_2)_a$ $\nu(CO_2)_s$	weak weak weak

Tanabe[14], Anderson and Rochester[15] and Ghiotti and Boccuzzi[16]. Curves I and II result from CO_3(I) and CO_3(II), respectively. The assignments of the bands obtained are represented in Table 1.

After spectrum (c) in Fig. 4 was recorded, the infrared cell was evacuated at ambient temperature (Ca. 800°C). The resulting spectrum was changed depending on the elapsed time as shown in Fig. 6. The species CO_3 (II) due to bands at 1620, 1270 and 980 cm^{-1} disappeared in 3 min, whereas the species CO_3 (I) remained even 200 min later. These results suggest that the species CO_3 (I) is more strongly adsorbed on the surface than the species CO_3 (II). Fig. 7 illustrates

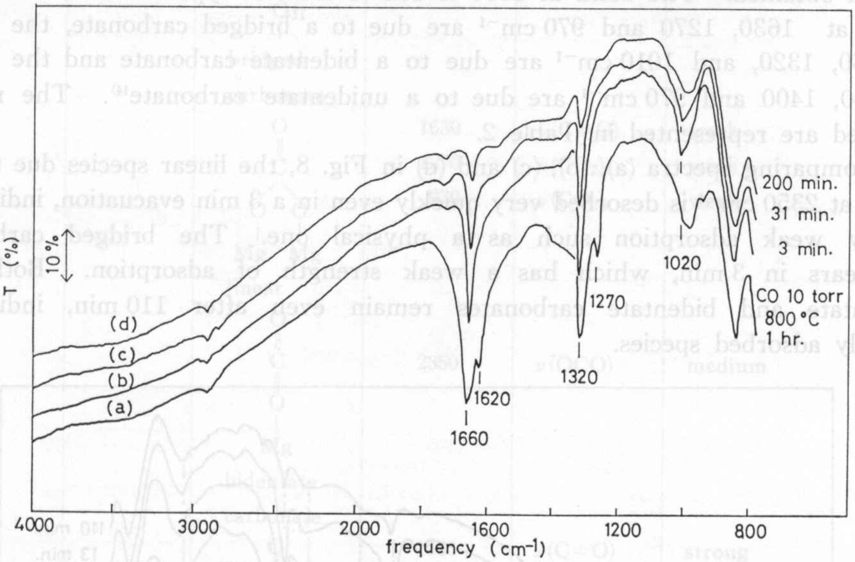


Fig. 6. IR spectra of CO adsorbed on S_{800} on evacuating the system.

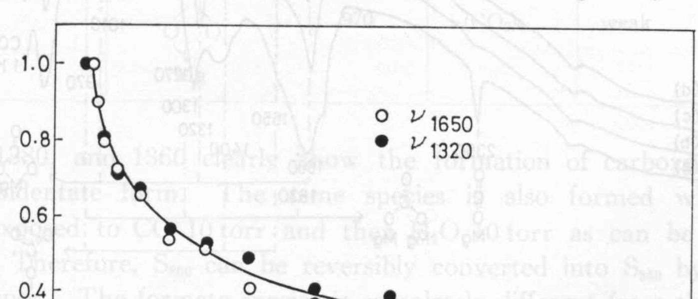


Fig. 7. Intensity change of the paired bands CO adsorbed on S_{350} in evacuating conditions.

the variation of the intensity ratio (I/Io) for the bands at 1650 and 1320 cm^{-1} at the elapsed time under the evacuation at 300°C. Both bands give the same locus, which demonstrates again the bands to have originated from the species CO_3 (I).

3-2. Adsorption of CO_2 on S_{800}

The adsorption of CO_2 on S_{800} gives various kinds of species, as has been demonstrated by a large number of investigators[11~13]. Fig. 8 illustrates the variation of the I. R. spectra of adsorbed CO_2 on S_{800} at 300°C, depending on the evacuation time. Four different species were identified by the analysis of the spectra obtained. The band at 2350 is due to a linear type carbon dioxide, the bands at 1630, 1270 and 970 cm^{-1} are due to a bridged carbonate, the bands at 1660, 1320, and 1010 cm^{-1} are due to a bidentate carbonate and the bands at 1550, 1400 and 970 cm^{-1} are due to a unidentate carbonate[14]. The results obtained are represented in Table 2.

Comparing spectra (a), (b), (c) and (d) in Fig. 8, the linear species due to the bands at 2350 cm^{-1} is desorbed very quickly even in a 3 min evacuation, indicating a very weak adsorption such as a physical one. The bridged carbonate disappears in 3 min, which has a weak strength of adsorption. Both the unidentate and bidentate carbonates remain even after 110 min, indicating strongly adsorbed species.

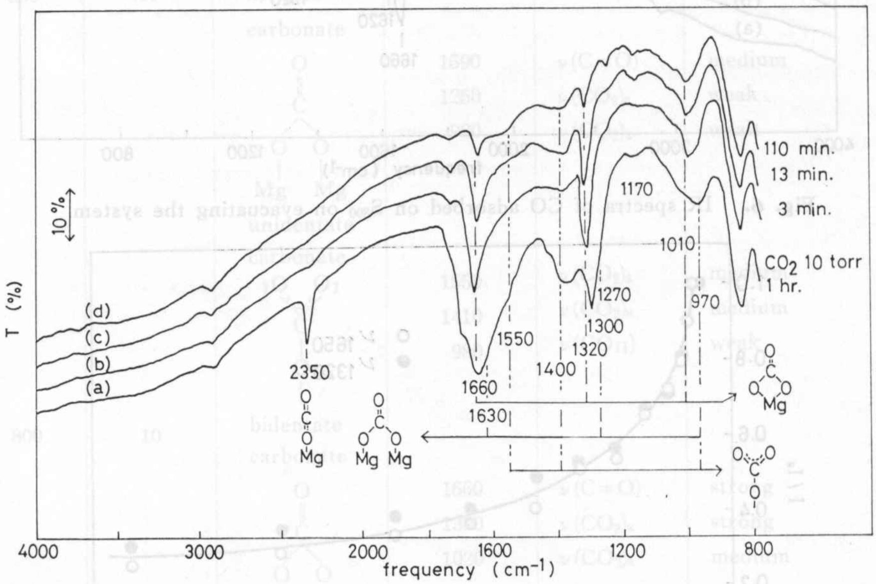
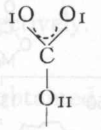
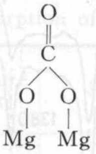
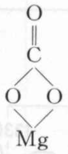


Fig. 8. Spectral changes for CO_2 adsorbed on S_{800} at various evacuating times.

3-3. Adsorption of CO on S_{350}

Commercially prepared magnesium oxide has a large number of hydroxyl groups on the surface. The hydroxyls show a variety of reactivity to ambient gases depending on the situation of the location of surface structures[17~19]. Fig. 9 shows the I. R. spectra of CO adsorbed on S_{350} {see spectrum (a)}. The bands at

Table 2. Wave number (cm^{-1}) of bands of carbonate after adsorption of CO_2 on S_{800}

Ads. temp. (°C)	Pressure (torr)	Species	frequencies (cm^{-1})	assignment	features
300	10	unidentate carbonate 	1550 1400 970	$\nu(O_ICO_I)_a$ $\nu(O_ICO_I)_s$ $\nu(CO_{II})$	medium medium weak
		bridged carbonate 	1630 1270 970	$\nu(C=O)$ $\nu(CO_2)_a$ $\nu(CO_2)_s$	weak weak weak
		linear 	2350	$\nu(OCO)$	medium
		bidentate carbonate 	1660 1320 970	$\nu(C=O)$ $\nu(CO_2)_a$ $\nu(CO_2)_s$	strong strong weak

2840, 1600, 1380, and 1360 clearly show the formation of carboxylate species which is a bidentate form. The same species is also formed when S_{800} is successively exposed to CO 10 torr and then H_2O 10 torr as can be seen from spectrum (b). Therefore, S_{800} can be reversibly converted into S_{350} by hydration with water vapor. The formate species is completely different from the bidentate carbonate formed on S_{800}, as can be seen from the spectrum (c).

In Fig. 9 (a) and (b), the band at 2840 cm^{-1} due to the CH stretching, and the bands at 1600, 1380 and 1360 cm^{-1} due to the asymmetric stretching of CO_2, the CH in-plane deformation and the symmetric stretching of CO_2 for formate ion are obtained. The formate species obtained on S_{350} can be confirmed by using the hydrated S_{800} with D_2O. Fig. 10 shows the comparison of the I. R. spectra on S_{800} obtained by two different types of water, H_2O-hydration or D_2O-hydration, then CO adsorption {see spectra (a) and (b)}. The broad band at around 3550 cm^{-1} due to OH groups in the spectrum (a) clearly shifts to the broad band at around 2760 cm^{-1} due to OD. The band at 2840 cm^{-1} due to the CH stretching shift to the band 2100 cm^{-1} due to the CD stretching. The band at 1600 cm^{-1} due to the asymmetric stretching CO_2 shows no change whereas the band at 1360 cm^{-1} due to the symmetric stretching CO_2 slightly

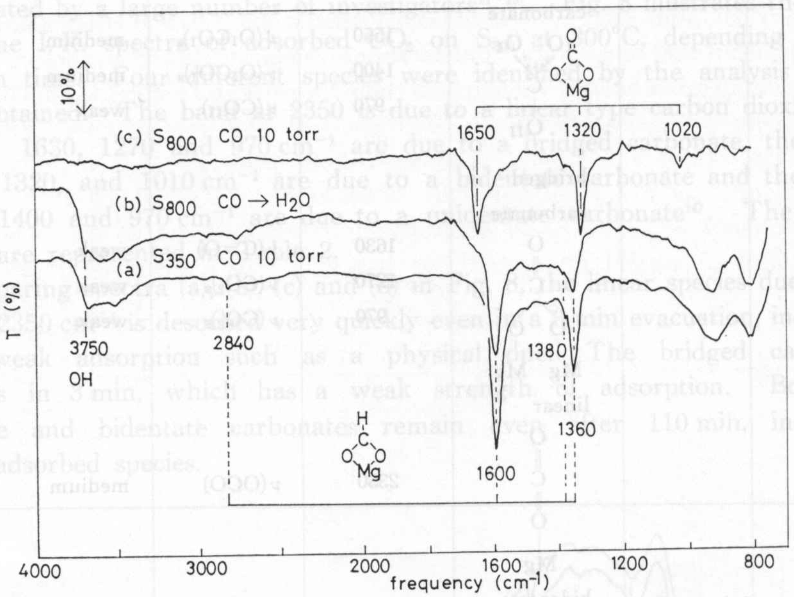


Fig. 9. Comparison of the CO adsorbed on S_{800}, S_{350} and hydrated S_{800}.

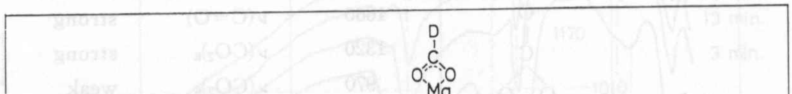


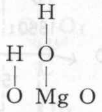
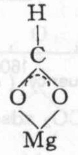
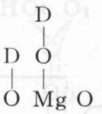
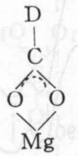
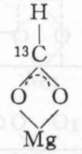
Fig. 10. Comparison of IR spectra of ^{12}CO and ^{13}CO adsorbed on S_{800} which was hydrated by D_2O or H_2O.

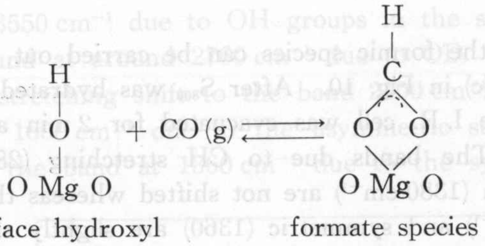
shifts to 1330 cm^{-1}.

Further reconformation for the formic species can be carried out by using ^{13}CO as shown in the spectrum (c) in Fig. 10. After S_{800} was hydrated by H_2O 10 torr for 10 min at 300°C, the I. R. cell was evacuated for 2 min and then ^{13}CO 10 torr was introduced. The bands due to CH stretching (2860 cm^{-1}) and the CH in-plane deformation (1380 cm^{-1}) are not shifted whereas the bands due to the asymmetric (1600 cm^{-1}) and symmetric (1360) are slightly shifted to 1550 and 1330 cm^{-1}, respectively. Table 3 shows the summary of the assignment of the bands obtained.

Based on the results obtained so far, one may propose the following adsorption scheme,

Table 3. Wave number of bands of formate and hydroxyls after adsorption of CO on S_{350} or hydrated S_{800}

Ads. Temp. (°C)	^{12}C, ^{13}C or surface hydroxyls	Pressure (torr)	Species	frequencies (cm^{-1})	assignment	features
300	OH	10		3750–3550	OH groups	medium
				2840	ν(CH)	weak
				1380	CH in-plane deformation	medium
				1600	$\nu(CO_2)_a$	strong
				1360	$\nu(CO_2)_s$	strong
	OD ^{12}C			2760–2550	OD groups	medium
				2100	ν(CD)	medium
				1600	$\nu(CO_2)_a$	strong
				1330	$\nu(CO_2)_s$	medium
	OH ^{13}C			2860	$\nu(^{13}CH)$	weak
				1380	^{13}CH in-plane deformation	medium
				1550	$\nu(CO_2)_a$	strong
				1330	$\nu(CO_2)_s$	medium


$$\begin{array}{c}\mathrm{H}\\|\\\mathrm{O}\\|\\\mathrm{O\,Mg\,O}\end{array} + \mathrm{CO(g)} \rightleftharpoons \begin{array}{c}\mathrm{H}\\|\\\mathrm{C}\\ \diagup\quad\diagdown\\ \mathrm{O}\qquad\mathrm{O}\\ \diagdown\quad\diagup\\ \mathrm{O\,Mg\,O}\end{array} \qquad (1)$$

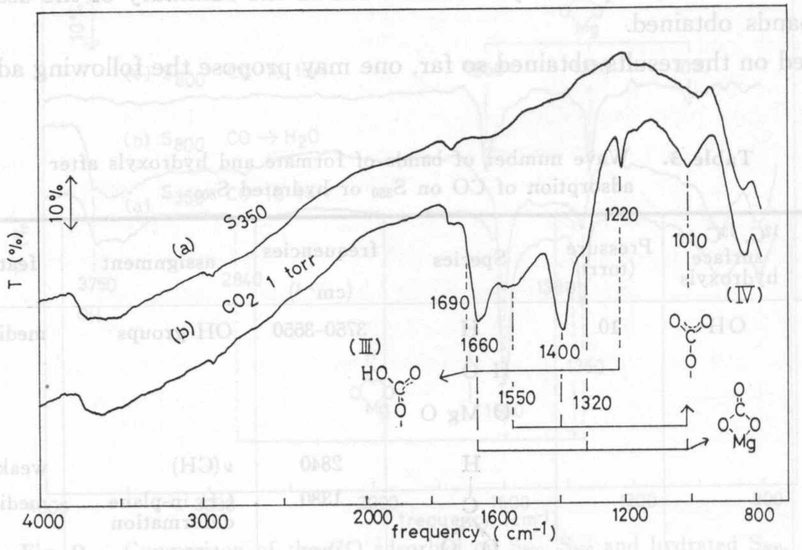


Fig. 11. IR spectra of CO_2 adsorbed on S_{350}.

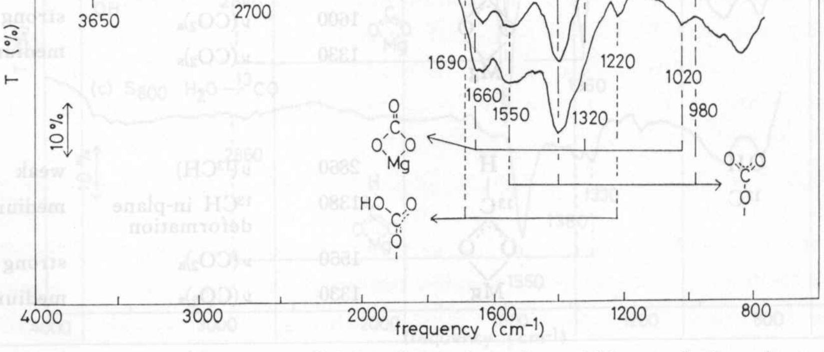


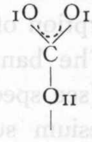
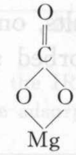
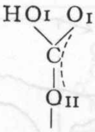
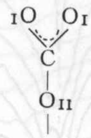
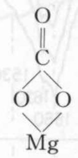
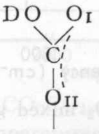
Fig. 12. IR spectra of CO_2 adsorbed on S_{800} which was hydrated by D_2O (a) or H_2O.

3–4. Adsorption of CO_2 on S_{350}

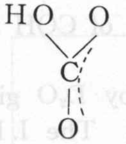
The infrared spectrum of CO_2 adsorbed on S_{350} was obtained at 300°C as shown in Fig. 11 (b) with the main bands at 1660 and 1400 cm^{-1} and the sharp band at 1220 cm^{-1}. The bands at 1550, 1440 and 1010 cm^{-1} are due to an unidentate carbonate species (species IV) and the bands at 1660, 1320, 1010 cm^{-1} are due to the bidentate carbonate species, (species I) and the bands at 1690 and 1220 cm^{-1} are due to the bicarbonate species (species III). The sharp band at 1220 cm^{-1} can be assigned to the bending vibration of COH as demonstrated by Lercher et al[14]. and Fimilinov et al[17].

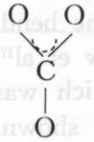
The adsorption of CO_2 on S_{800} which was hydrated by D_2O gives useful information in assigning the species as shown in Fig. 12. The I. R. spectra

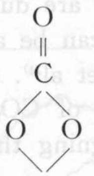
Table 4. Wave number of bands of carbonate and hydroxyls after adsorption of CO_2 on S_{800}

Ads. Temp. (°C)	surface hydroxyls	Pressure (torr)	Species	frequencies (cm^{-1})	assignment	features
300	OH	10		1550 1400 980	$\nu(O_ICO_I)_a$ $\nu(O_ICO_I)_s$ $\nu(CO_{II})$	medium strong medium
				1660 1320 1010	$\nu(CO)$ $\nu(CO_2)_a$ $\nu(CO_2)_s$	strong weak medium
				1690 1220	$\nu(O_ICO_{II})_a$ COH bending vibration	weak medium
	OD	10		2700–2450	OD groups	medium
				1550 1400 980	$\nu(O_ICO_I)_a$ $\nu(O_ICO_I)_s$ $\nu(CO_{II})$	medium strong weak
				1660 1320 1010	$\nu(CO)$ $\nu(CO_2)_a$ $\nu(CO_2)_s$	strong medium weak
				1690 960	$\nu(CO_2)_a$ COD bending vibration	weak weak

obtained at the two samples hydrated by H_2O and D_2O were compared. Some I. R. bands due to bicarbonate species (III) on the D_2O-hydrated S_{800} shift clearly, such as from 1220 to 960 cm^{-1} whereas no shift is observed for the carbonate species. The assignments of the bands are presented in Table 4. These results clearly show the formation of three different carbonate species according to the adsorption of CO_2 on S_{350}, shown as follows,


(III)


(IV)


(I)

3-5. Adsorption of CO-CO_2 mixture on S_{800}

Our interest is focused on the adsorption behavior of CO-CO_2 mixture. Fig. 13 illustrates the I. R. spectra of CO adsorbed on S_{800} {see spectrum (b)} compared to the spectra (c)～(d), which were obtained by the successive addition of CO_2 into the I. R. cell under the same condition. All the bands are very similar to ones obtained at the single adsorption of CO_2 on S_{800}. This comparison of the IR spectra is done in Fig. 14. The band at 2350 cm^{-1} was not found in the spectrum of the CO-CO_2 mixture {see spectrum (b)}, because it may have resulted from no vacant space of magnesium surface ions for the linear type adsorbed species of CO_2. From these results, one may recognize that the single gas adsorption of CO_2 gives the same adsorbed species as those of the CO-CO_2 mixed gas adsorption.

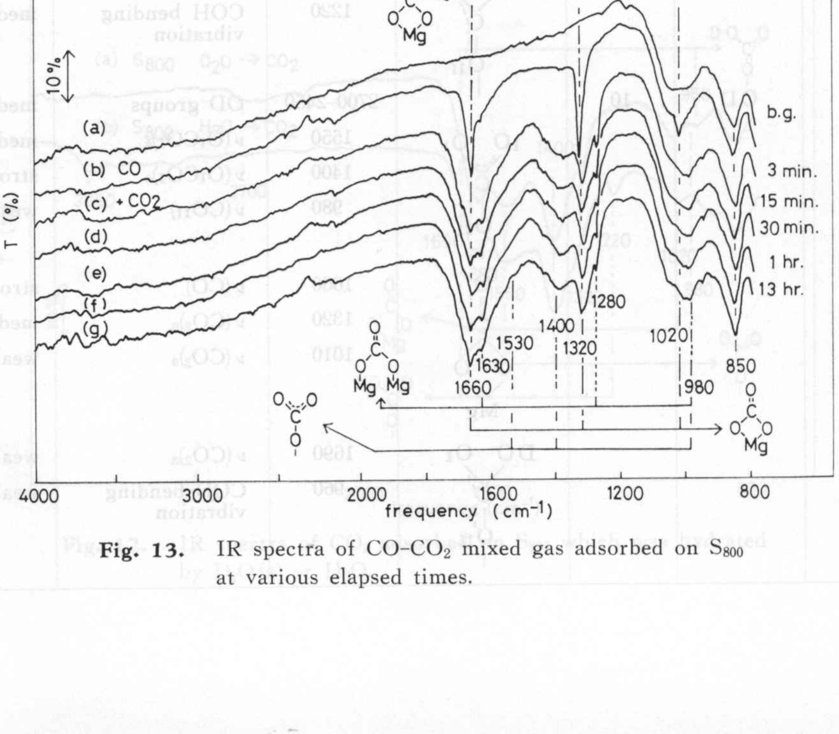


Fig. 13. IR spectra of CO-CO_2 mixed gas adsorbed on S_{800} at various elapsed times.

The desorption of the carbonate species adsorbed in the CO-CO_2 mixture gives a characteristic spectra as shown in Fig. 15. After a 10 min evacuation, the spectrum (c) gives only the carbonate species (I) which coincides with the spectrum of CO adsorbed on S_{800} {see Fig. 4 (a)}. These results clearly demonstrate that each gas in the CO-CO_2 mixture adsorbs on S_{800} to form the same species as in the case of single adsorption, except the linear species. The species is assigned to be the bidentate carbonate characterized by the bands at 1660,

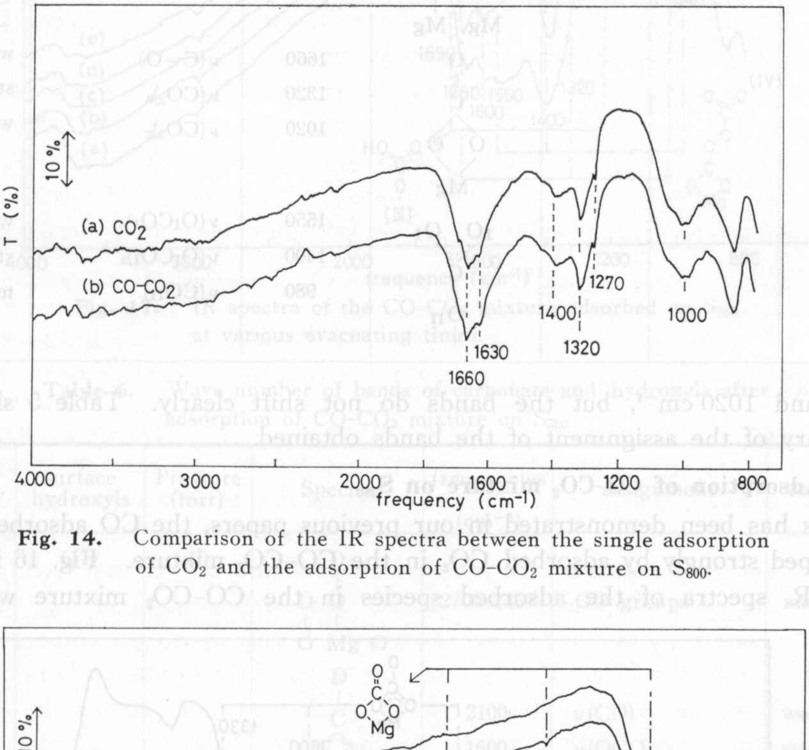


Fig. 14. Comparison of the IR spectra between the single adsorption of CO_2 and the adsorption of CO-CO_2 mixture on S_{800}.

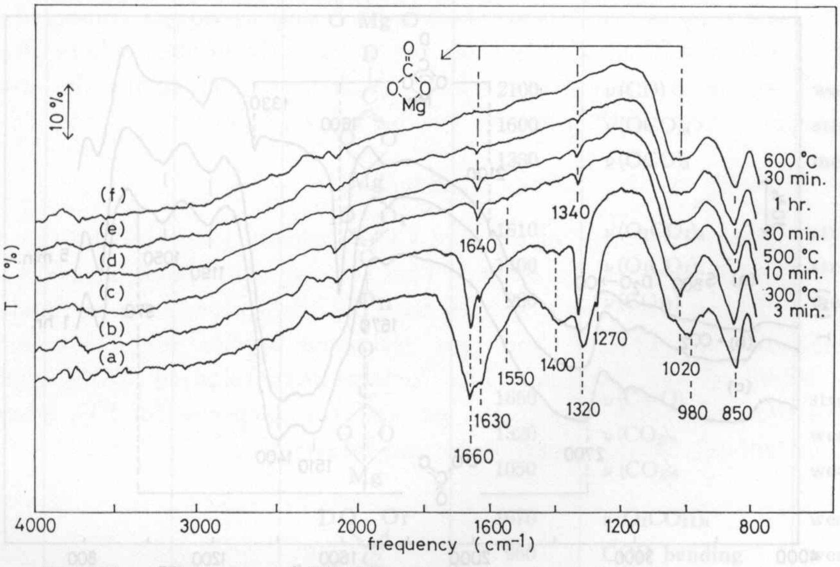
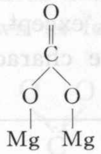
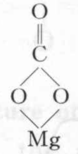


Fig. 15. IR spectra of CO-CO_2 mixed gas adsorbed on S_{800} at various evacuation temperatures and times.

Table 5. Wave number of bands of carbonate and hydroxyls after adsorption of CO–CO_2 mixture on S_{800}

Ads. Temp. (°C)	surface hydroxyls	Pressure (torr)	Species	frequencies (cm^{-1})	assignment	feature
300	none	10		1630 1270 980	$\nu(C=O)$ $\nu(CO_2)_a$ $\nu(CO_2)_s$	weak weak weak
				1660 1320 1020	$\nu(C=O)$ $\nu(CO_2)_a$ $\nu(CO_2)_s$	weak strong weak
				1550 1400 980	$\nu(O_ICO_I)_a$ $\nu(O_ICO_I)_s$ $\nu(CO_{II})$	weak strong medium

1320 and 1020 cm^{-1}, but the bands do not shift clearly. Table 5 shows the summary of the assignment of the bands obtained.

3-6. Adsorption of CO-CO_2 mixture on S_{350}

As has been demonstrated in our previous papers, the CO adsorbed on S_{350} is trapped strongly by adsorbed CO_2 in the CO-CO_2 mixture. Fig. 16 illustrates the I. R. spectra of the adsorbed species in the CO-CO_2 mixture which are

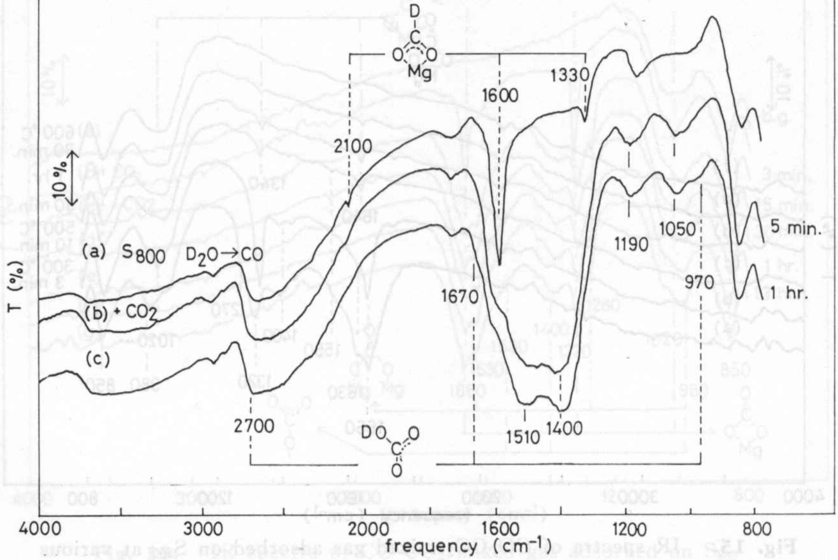


Fig. 16. IR spectra of CO+CO_2 adsorbed on S_{800} which was hydrated by D_2O.

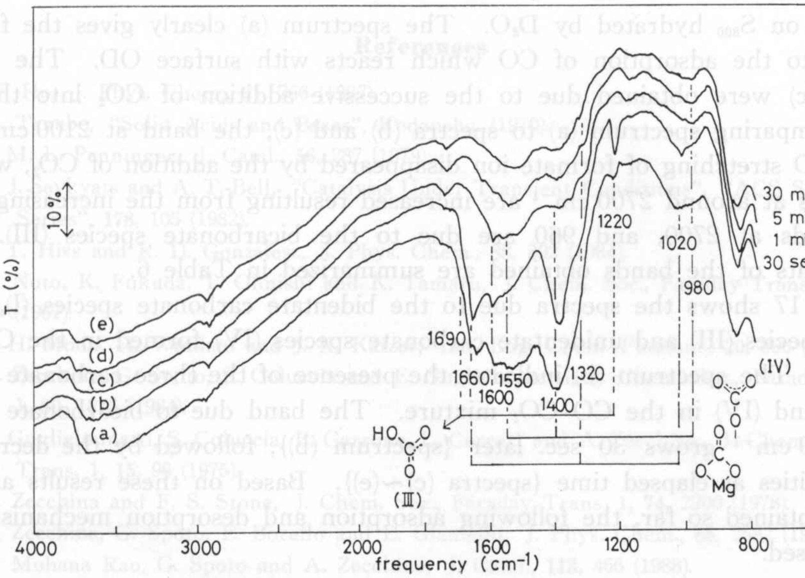
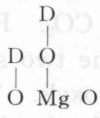
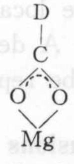
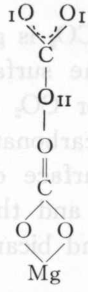
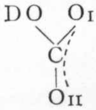


Fig. 17. IR spectra of the CO–CO_2 mixture adsorbed on S_{350} at various evacuating times.

Table 6. Wave number of bands of carbonate and hydroxyls after adsorption of CO–CO_2 mixture on S_{350}

Ads. Temp. (°C)	surface hydroxyls	Pressure (torr)	Species	frequencies (cm^{-1})	assignment	feature
300	OD	10		2700–2450	OD groups	medium
				2100	ν(CD)	weak
				1600	$\nu(OCO)_a$	strong
				1330	$\nu(OCO)_s$	medium
				1510	$\nu(O_ICO_I)_a$	strong
				1400	$\nu(O_ICO_I)_s$	strong
				980	$\nu(CO_{II})$	medium
				1660	ν(C=O)	strong
				1320	$\nu(CO_2)_a$	weak
				1050	$\nu(CO_2)_s$	weak
				1670	$\nu(O_ICO_{II})_a$	weak
				960	COD bending vibration	weak

adsorbed on S_{800} hydrated by D_2O. The spectrum (a) clearly gives the formate ion due to the adsorption of CO which reacts with surface OD. The spectra (b) and (c) were obtained due to the successive addition of CO_2 into the I. R. cell. Comparing spectrum (a) to spectra (b) and (c), the band at 2100 cm^{-1} due to the CD stretching of formate ion disappeared by the addition of CO_2, whereas the bands at around 2700 cm^{-1} are increased resulting from the increasing COD. The bands at 2700, and 960 are due to the bicarbonate species (III). The assignments of the bands obtained are summarized in Table 6.

Fig. 17 shows the spectra due to the bidentate carbonate species (I), bicarbonate species (III) and unidentate carbonate species (IV) formed in the CO-CO_2 mixture. The spectrum (b) indicates the presence of the three carbonate species (I), (III) and (IV) in the CO-CO_2 mixture. The band due to bicarbonate species (III), 1220 cm^{-1} grows 30 sec. later {spectrum (b)}, followed by the decrease in its intensities at elapsed time {spectra (c)～(e)}. Based on these results and the resulst obtained so far, the following adsorption and desorption mechanism may be proposed.

$$\text{one carboxylate} \xrightarrow{+2OH} \xrightarrow{+2CO_2} \text{three bicarbonates} \xrightarrow{-2CO_2} CO(g)+3OH$$

3-7. Characterization of Adsorbed Species

The forms of carbonate species adsorbed on magnesium oxide are greatly influenced by the amounts of surface hydroxyls and the concentration of CO and CO_2 as adsorbates. The thermal dehydration of MgO clearly shows the differences of the surface carbonate species formed on S_{350} and S_{800}. The surface hydroxyls are very reactive with CO and CO_2. From the Tables 1～6, one may recognize the clear differences between the two surfaces S_{350} and S_{800}, which are clearly characterized by the surface hydroxyls. The hydroxyls control the distribution of CO and CO_2 adsorbed on the local surface sites, where the sites are located on corners, steps or terraces. A detailed analysis for the structure of the trapping effect of CO_2 on CO will be reported later.

4. Conclusions

The adsorption behavior of CO and CO_2 is greatly influenced by the degree of dehydration of magnesium oxide. The surface dehydrated at 800°C gives mainly four different carbonate species for CO_2 adsorption, such as unidentate, linear, bidentate and bridged, and two carbonate species for CO adsorption, such as bidentate and bridged. The surface dehydrated at 350°C gives one species for CO adsorption, a formate ion and three species for CO_2 adsorption such as unidentate, bidentate carbonate and bicarbonate.

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