Characterization of the Surface of Alkali Metal-modified MgO by IR spectroscopy

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Abstract

CO_2 gas was employed to characterize the surface of alkali metal-modified MgO by IR spectroscopy. Doses of alkali metals changed the composition of CO_2-derived species because of the enchanced basicity of the surfaces. Li showed the highest modification effect of the three alkali metals used; this result was in the reverse order of electron-donating ability. Taking inso account the fact that Li^+ can be substituted for Mg^{2+} due to their similar sizes, and that alkali metal oxide and hydroxide were shown by XRD patterns, the existence of an Li site strongly-connected with oxygen was considered. The data from both IR spectra and TPD profiles leads to the possibility of quantitative evaluation of basicity of the surface only by IR spectroscopy to a certain degree.

1. INTRODUCTION

Magnesium oxide is a basic material which is frequently reported as catalysts and ceramics, etc. A large number of researches concerning metal-doped MgO have been also made in terms of the changes of surface structures[1] and of catalytic activities[2,3].

Doses of alkali-metals onto MgO increase the basicity due to their electron donating ability[4]. Kijeński et al.[5] reported the formation of superbasic sites ($H_- > 35$) by evaporating sodium onto MgO. Doping of 1wt% of alkali metal compounds in MgO enhanced the isomerization activity of 1-butene and doping of 10wt% decreased it remarkably[6].

In this report, the modification effect of three alkali metals on MgO was compared by changes of IR spectra after exposure of CO_2. We also made an attempt of quantitative evaluation of basicity by these changes, with the help of the TPD profiles.

2. EXPERIMENTAL

(1). Preparation of the Samples.

10 g of MgO powder (Merck Corp.) was suspended by redistilled water of 200 ml with three-time decantations. This suspension was dried on a hot plate under agitation and put in an oven at 363 K overnight. The starting material for addition of alkali metal was aqueous alkali-hydroxide (Special Grade, Wako Pure Pharmaceutical Corp.) solution; the added weight was 1, 5 or 10% to MgO.

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(2). IR spectroscopy

The same equipments as in the previous paper[7] was used. The cell was composed of the portion for preheating which was made of quartz glass, and that for IR measurment, which was made of Pyrex glass with KBr windows.

Prior to the measurement, the compressed IR disk of 20 mm in diameter was put in the cell, and pretreated at 723 K for Li-doped, and at 623 K for K- and Cs-doped MgO at which each alkali metal-hydroxide decomposes, respectively. All the samples were evacuated at 1073 K for 3 hrs.

The CO_2 gas was commercially prepared by Takachiho Chem. Corp., the purity of which was 99.99%.

(3). XRD Technique

The equipment for obtaining XRD patterns was Rigaku RAD-3R. The line source was Cu and scanning speed was 1°/min. Measurement was done at room temp. in air.

3. RESULTS AND DISCUSSION

3-1 XRD patterns.

Fig. 1 shows the XRD partterns of MgO and alkali metal-modified samples after exposure of an He gas flow at 1073 K, where the parenthesized numbers are the weight % of added alkali metal to MgO. The existences of lithium hydroxide and oxide were shown in Li (1) and Li (5)-MgO, while the patterns of neither hydroxides nor oxides were found for K - and Cs-doped samples. These results may reflect upon stronger interaction of Li with lattice oxygen than of K or Cs, although this idea may be an indirect evidence.

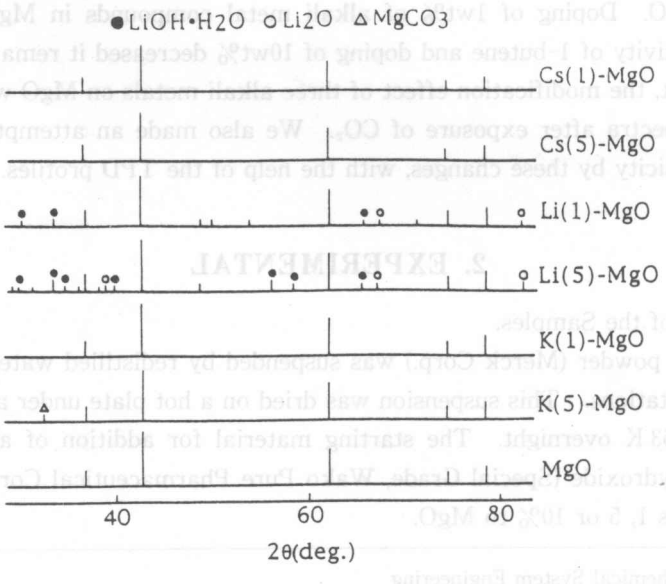

Fig. 1 XRD patterns after He treatments at 1073 K.

3-2 Adsorption Properties of CO_2 on Various Alkali Metal-doped MgO.

Figs. 2, 3 and 4 show the IR spectra on various alkali metal-doped MgO after exposure of 5 Torr-CO_2 at room temp. followed by raising to 573 K. Primary species on MgO were bidentate carbonate (designate as bi. c.) at 1668, 1632, 1316, 1281 cm^{-1} and linear CO_2 at 2354 cm^{-1} while the intensities of unidentate carbonate (designate as uni. c.) at 1536, 1390-1380 and 1567-1561, 1399-1396 cm^{-1} increased for K- and Cs-doped samples, respectively. Li (1)-MgO showed the most prominent change of all the alkali metal-doped samples; bi. c. and linear CO_2 almost disappeared and the intensity of uni. c. increased distinctively.

Alkali metal-CO_2 complexes and carbonates reported by Kafafi et al.[5] are shown by Table 1. They mentioned that these complexes were not stable at higher than 300 K and were converted into alkali metal carbonates. Because these carbonates were not found in our results, the IR spectra we observed must be ascribed to the species not on alkali metals but on MgO.

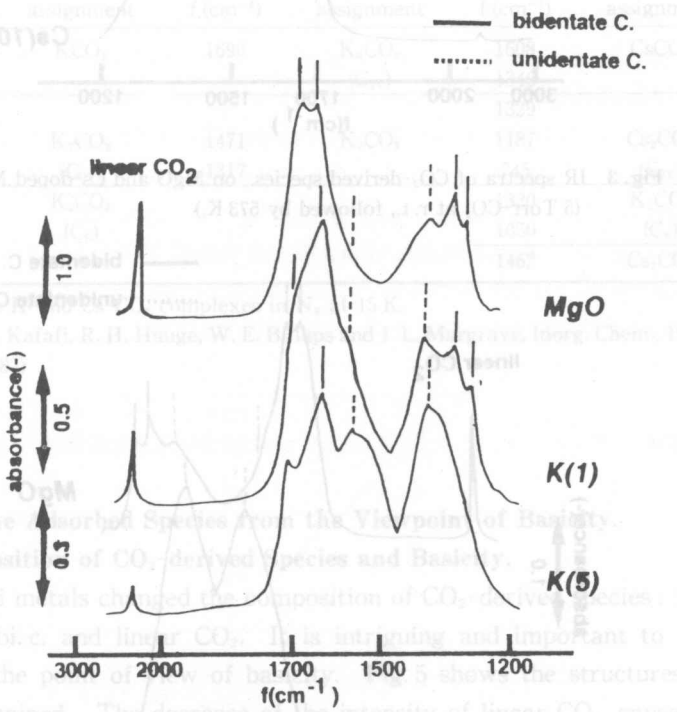

Fig. 2 IR spectra of CO_2-derived species on MgO and K-doped MgO. (5Torr-CO_2 at r. t., followed by 573 K.)

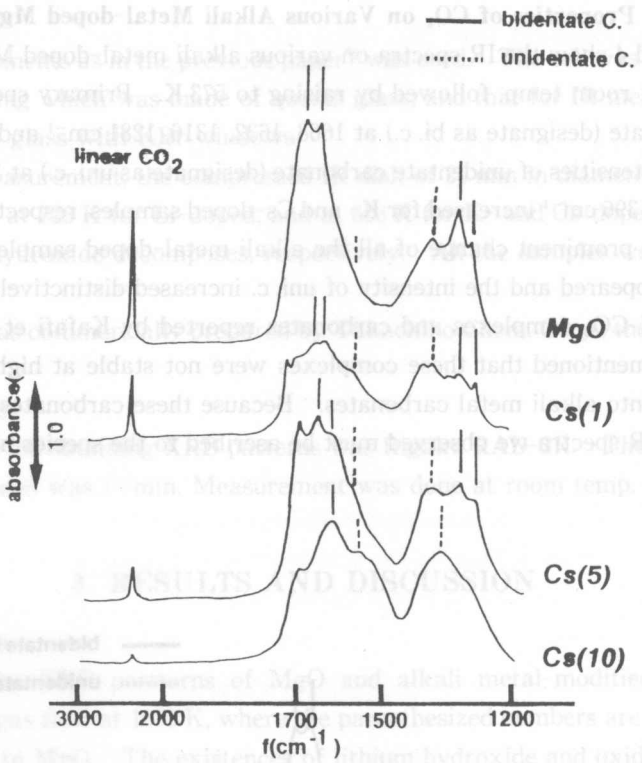

Fig. 3 IR spectra of CO_2-derived species., on MgO and Cs-doped MgO. (5 Torr-CO_2 at r. t., followed by 573 K.)

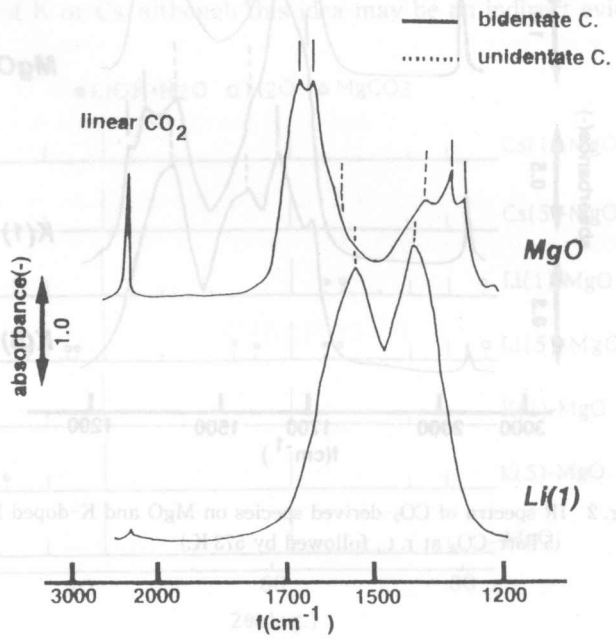

Fig. 4 IR spectra of CO_2-derived species., on MgO and Li-doped MgO. (5 Torr-CO_2 at r. t., followed by 573 K.)

Table 1 IR frequencies of alkali metal-CO_2 complexes and carbonates.

f (cm^{-1})	assignment	f (cm^{-1})	assignment	f (cm^{-1})	assignment
1575		1756		1448	
1570		1751		984	Li_2CO_2
1569	$LiCO_2$	1221	$LiCO_2$	566	(C_S)
1330	(C_{2v})	1209	(C_S)		
1305		740		1969	LiC_2O_4
807		612		1160	(C_{2v})
799		599			
533		1662			
520		1316	$Li_2C_2O_4$	1465	Li_2CO_3
		807		865	
		498			

Table 1. The Li-CO_2 complexes in Ar at 15 K.
(Z. H. Kafafi, R. H. Hauge, W. H. Billups and J. L. Margrave, J. Am. Chem. Soc., 1983, **105**, 3886-3793.)

$$Li \times CO_2 \longrightarrow LiCO_2(CO_2)_x + Li \longrightarrow Li_2C_2O_4 \xrightarrow{T>>300K} Li_2CO_3 + CO$$

f (cm^{-1})	assignment	f (cm^{-1})	assignment	f (cm^{-1})	assignment
1510	KCO_2	1690	K_nCO_2	1608	$CsCO_2$
			(C_{2v})	1346	
1342				1329	
1184	K_2CO_2	1471	K_2CO_3	1187	Cs_2CO_2
739	(C_{2v})	1317		745	(C_{2v})
1329	K_2CO_2			1320	K_2CO_2
1052	(C_S)			1050	(C_S)
				1462	Cs_2CO_3

Table 2. The K-and Cs-CO_2 complexes in N_2 at 15 K.
(Z. H. Kafafi, R. H. Hauge, W. E. Billups and J. L. Margrave, Inorg. Chem., 1984, **23**, 177-183)

3-3 Change in the Adsorbed Species from the Viewpoint of Basicity.

3-3-1 The Composition of CO_2-derived Species and Basicity.

Doses of alkali metals changed the composition of CO_2-derived species; favored uni. c. with decrease of bi. c. and linear CO_2. It is intriguing and important to look at these phenomena from the point of view of basicity. Fig. 5 shows the structures of the CO_2-derived species obtained. The decrease of the intensity of linear CO_2, caused by doses of alkali metals, indicates the decrease of acidity from the fact that the acidic site (Mg^{2+}) is responsible for the formation of linear CO_2[4]. Taking into account the difference of structures of two carbonates, furthermore, it would be reasonable that the contribution of the basic site (O^{2-}) to uni. c. is larger than to bi. c. because uni. c. doesn't have a direct ligand to the acidic site. Alkali metals, therefore, work to produce uni. c. due to increasing electron density of surface lattice exygen: basicity.

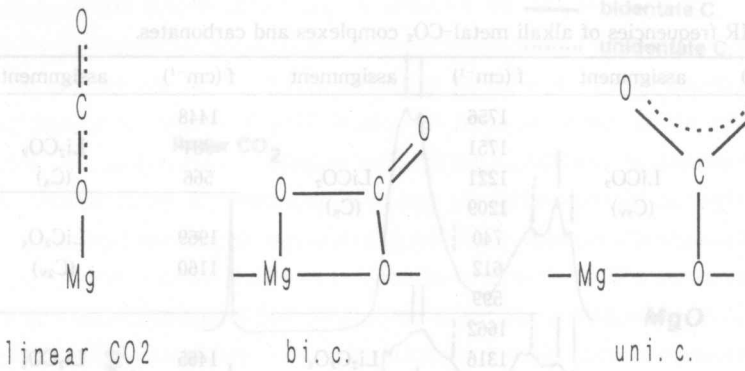

Fig. 5 Structures of CO_2-derived species on MgO and alkali metal-doped MgO.

3-3-2 IR Frequency and Basicity.

The increase of basicity is accompanied by the decrease in $\Delta\nu$: difference of the IR frequencies of asym. and sym. stretching vibrations of OCO of uni. c. Lercher et al.[6] and Philipp et al.[7] reported this correlation on MgO/Al_2O_3 and MgO/CaO, respectively. Their results are shown by Fig. 6, which are the plots of $(\Delta\nu)^{-1}$ vs. molar ratio of MgO in mixed oxides. On MgO/Al_2O_3 (a), the mixture of basic and acidic materials, $(\Delta\nu)^{-1}$ increased with the concentration of MgO linearly, showing a reasonable parameter for evaluating basicity. On the mixture of two basic materials (b), the component which has the maximum value was seen to exist.

Similar estimation was made for alkali metal-doped MgO in Table 2. Li-doped MgO showed the highest of all the samples; this tendency was the same as the change of the composition of CO_2-derived species in the previous section.

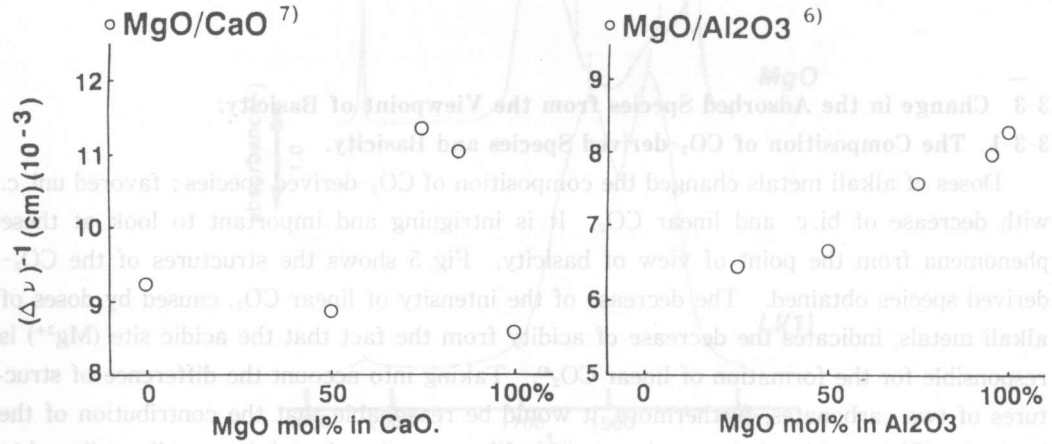

Fig. 6 Correlation of $(\Delta\nu)$-1 with basicity.

Table 3. Estimation of surface basicity of alkali metal doped MgO by IR frequencies of uni. c.

	asym. (cm^{-1})	sym. (cm^{-1})	$\Delta\nu^{-1}(\times 10^{-3})$(cm)
MgO	1563	1374	5.29
Cs(1)	1561	1380	5.52
Cs(5)	1567	1380	5.35
Cs(10)	1551	1364	5.35
K(1)	1563	1387	5.68
K(5)	1548	1370	5.62
Li(1)	1538	1406	7.58

$\Delta\nu = \nu_{asym.} - \nu_{sym.}$ of OCO of unidentate carbonate

3-3-3 Correlation of $(\Delta\nu)^{-1}$ with the TPD Profile.

Correlation of $(\Delta\nu)^{-1}$ with the TPD profiles[8] was examined in Fig. 7. To evaluate basicity quantitatively, the TPD data were replaced by the ratio of the desorbed amounts of CO_2 at highter temperature than 673 K to the total one. (R), Two parameters in the figure showed correlation. This result may lead to the idea that both parameters can give us the similar information concerning basicity of the surface of MgO. The increase in $(\Delta\nu)^{-1}$ of 2×10^{-3} corresponds to that in about 6×10^{-6}mol-CO_2/m^2 desorbed at higher temp., namely located on the strong basic sites and this increase equals about 0.3 of surface coverage based on (100) surface.

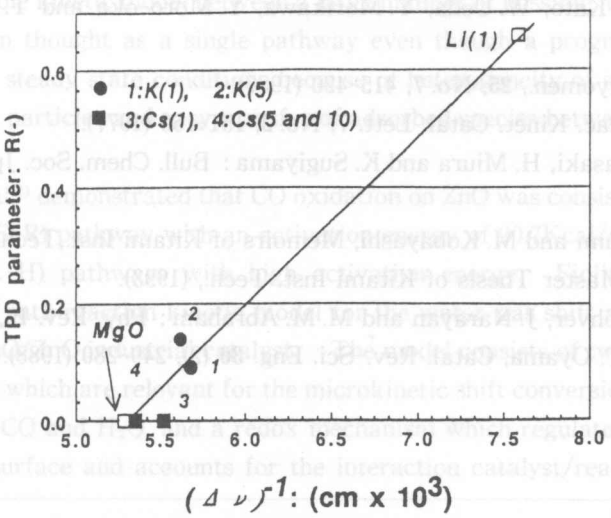

Fig. 7 Correlation of the basicity evaluated by the two parameters.

3-3-4 The Extraordinarily High Modification Effect of Li.

Both parameters from the IR spectra and the TPD profiles consistently showed the Li's much highest value of all the samples. Ionization potential cannot be the primary factor to cause this result, for its electron donating ability is the lowest of the three alkali metals, leading to the least contribution.

The second factor to be note is ion size. The ion size of Li is 0.68Å which is comparable to that of Mg^{2+} (0.60Å). Chen et al.[9] suggested the existence of Li^+-O^- which was formed by the substitution for Mg^{2+}, and this site was said to be active for oxidative coupling of methane[10]. Our results including XRD data, in which alkali metal oxide and hydroxide were found in Li-doped MgO as opposed to K- and Cs-doped ones, may also indicate the existence of such a site as strongly-interacting lithium-oxygen contributing to high basicity.

4. CONCLUSIONS

Comparison of modification effect of the three alkali metals on MgO was made and the conclusions were derived as follows;

(1). Li's much high modification effect was observed and ascribed to the Li-oxygen site substituted for Mg^{2+}.

(2). The quantitative evaluation of basicity was attempted by IR spectroscopy and was found to be possible by correlating with the TPD profiles.

References

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