Correlation of the Surface Basicity of Alkali Metal-Modified MgO Evaluated by the Two Parameters

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Synopsis. The surface basicity of alkali metal-modified MgO was evaluated by both TPD and IR techniques and a good correlation between the two results was obtained, in which Li showed the distinct modification effect on MgO.

The alkali metal has been used as a typical modifier of metals and metal oxides, because a dose of the alkali metal enhances electron-donating ability of lattice oxygen, that is to say, basicity. What intrigues us here is a quantitative aspect of changes in basicity by doping alkali metals. A number of methods for evaluating the basicity of solids have been suggested so far; one of them frequently used is exposure to CO_2 gas as a probe. We employed two techniques, IR (infrared) spectroscopy and TPD (temperature programmed desorption) technique for doing this, and our object in this paper is to correlate the two results.

Doses of alkali metals were done by adding aqueous alkali hydroxide solutions into MgO suspended in redistilled water, and then the sample was evaporated on a hot plate and dried in an oven at 363 K overnight. TPD spectra of CO_2 was obtained in an He stream after exposure to a CO_2-gas flow at 573 K for 3 h, using a tubular flow reactor made of quartz glass. IR measurement was done by a conventional transmission spectroscopy with a thin sample-disk of 20 mm in diameter. The sample was pretreated at 1073 K for 3 h in an He stream for TPD and in vacuo for IR measurement.

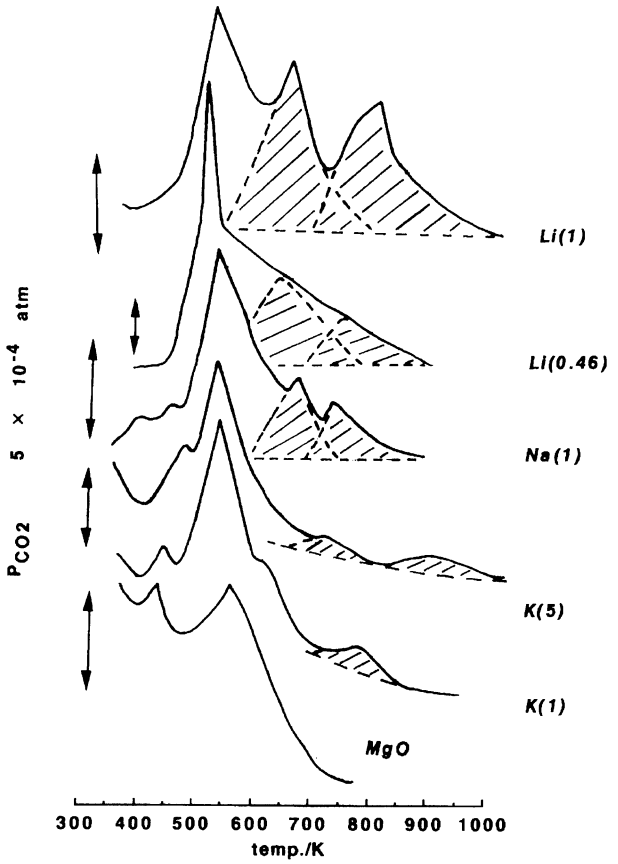

Fig. 1. TPD spectra in He after exposure to a CO_2 stream at 573 K for 3 h. (sample wt: 1.0 g, flow rate: 100 ml min^{-1}, rate of rising temp: 3 K min^{-1})

Figure 1 shows TPD profiles of CO_2 on MgO and alkali metal-modified MgO, where the parenthesized numbers mean the wt% of the doped alkali metal to MgO. One can see that doses of alkali metals increase the amount of desorbed CO_2 at higher temperature as well as the total one. Doses of Li and Na, in particular, gave rise to two peaks at higher temperature than 673 K, which did not appear on non-doped MgO. K(1)- and K(5)-MgO showed the similar tendency although this tendency was less clearer. The profiles for Cs-doped MgO, which are not shown in this figure, were almost the same as non-doped MgO.

The distribution of basic sites can be evaluated in terms of the temperature at which CO_2 desorbs; the higher is it, the stronger is the basicity.[1,2] From the graphical integration of the TPD spectra, the amount of CO_2 (shaded area in Fig. 1) desorbed at higher temperature than 673 K per the total one, thus, $q_{\text{higher temp}}/q_{\text{total}}$ was chosen to a parameter, which we call *TPD parameter*, for the first evaluation of basicity. As is easily seen from the orginal data (Fig. 1), Li(1) showed much the highest value of the six samples used.

For the second parameter, we would like to use the data from IR spectra of CO_2-derived species. Tanabe

Table 1. IR data of Unidentate Carbonate[a)]

Sample	Asym./cm^{-1}	Sym./cm^{-1}
Li (1)	1538	1406
Li (0.46)	1555	1406
Na (1)	1547	1385
K (5)	1548	1370
K (1)	1563	1387
Cs (10)	1551	1364
Cs (5)	1567	1380
Cs (1)	1561	1380
MgO	1563	1374

a) Asym. and Sym.: IR frequencies of OCO asymmetric and symmetric str. vib. of unidentate carbonate.

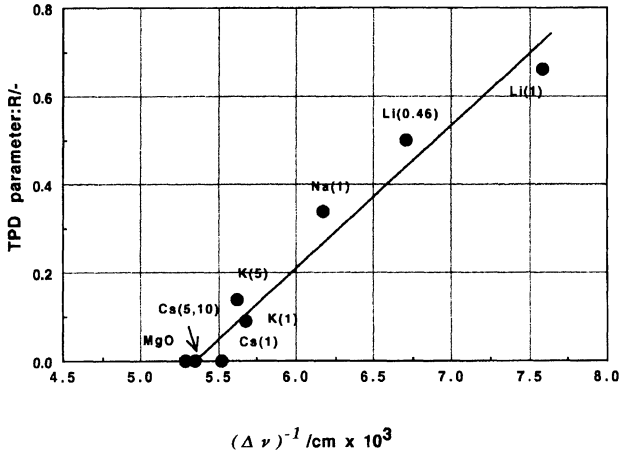

Fig. 2. Correlation of the basicity evaluated by the two parameters. R: $q_{\text{higher temp}}/q_{\text{total}}$. $\Delta\nu$: wavenumber difference of asym. and sym. str. vib. of O–C–O of unidentate carbonate.

et al.[3] reported that the partial charge of oxygen on metal oxides: δ_o was correlated with $\Delta\nu$: the difference of the IR frequencies between asymmetric and symmetric stretching vibration of unidentate carbonate (uni.c.); the decrease of $\Delta\nu$ was accompanied by the increase of δ_o, leading to the enhancement of basicity. On Mg O/Al_2O_3[4] and MgO/CaO[5] mixed oxides, furthermore, $\Delta\nu$ was found to depend on the make-up of each sample and these diversified $\Delta\nu$ were ascribed to changes in the surface basicity. We designate reciprocal $\Delta\nu$: $(\Delta\nu)^{-1}$ as *IR parameter*. Table 1 shows the IR frequencies of OCO asymmetric and symmetric stretching vibration of uni. c. observed after exposure of 5 Torr-CO_2 at room temp (1 Torr=133.322 Pa), followed by raising to 573 K.

What we attempt to do is correlating these two parameters mentioned above for alkali-doped MgO and the result is shown in Fig. 2. Plots of *TPD parameter* vs. *IR parameter* gave a linearity. This correlation leads to the fact that *TPD parameter* may reflect upon basicity qualitatively as well as quantitatively. This parameter must, in other words, take the average strength of basicity of the surfaces with many kinds of basic sites of diversified strength. $(\Delta\nu)^{-1}$, furthermore, results in ranging from $5.29—7.58\times10^{-3}$ under the change in R of 0.66, corresponding to the increase of 6.93×10^{-6} mol-CO_2 (desorbed at higher temp)/m^2. This estimated value is comparable with the datum for MgO by Choudhary and Rane:[2] not more than 10×10^{-6} mol m^{-2} desorbed at 573 K and higher.

One thing to note is, again, that Li showed the prominent effect on MgO of four alkali metals. The reason of the much enhanced basicity of MgO, caused by a dose of Li, has not been clarified, but the contribution of genisis of the Li-substituted sites due to similar sizes of Li^+ (0.068 nm) and Mg^{2+} (0.066 nm) may be considered.

References

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