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The Differences in Surface and Catalytic Properties of Two Magnesium Oxides Prepared from the Hydroxide and the Carbonate Hydroxide

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Two kinds of MgO were prepared; MgO(I) from magnesium hydroxide and MgO(II) from magnesium carbonate hydroxide by evacuating at various temperatures and their surface and structural properties and catalytic actions for alkylation and isomerization reactions were examined. IR spectra of CO_2 retaining or adsorbed showed broad bands on MgO(II), but relatively sharp bands on MgO(I). In the alkylation of phenol with methanol over MgO(I), phenol was selectively alkylated at the *ortho* positions to produce *o*-cresol and 2,6-xylenol. The *ortho*-selectivity of MgO(I) was higher than 96%, while that of MgO(II) was about 75%. A low selectivity of MgO(II) was considered to be caused by a heterogeneity of surface structure of MgO(II), which was suggested by broad IR bands of CO_2 species on MgO(II). For the isomerization of 1-butene, both of MgO became active when evacuated at 450 °C and showed maximum activities when evacuated at 600 °C. The activity and the selectivity (ratio of *cis*-2-butene to *trans*-2-butene) of both catalysts were not much different. However, for the isomerization of *cis*-2-butene, the maximum activity and the selectivity (ratio of *trans*-2-butene to 1-butene) of MgO (I) were about four times higher than those of MgO(II).

The catalytic properties are generally recognized to be dependent on the preparation method. The preparation consists of various factors which determine the property of the final product. These include precipitation method, aging period, washing way, calcining condition *etc*. Among these are kind of starting material and pretreatment condition which give often large effect on catalytic property.

The catalytic properties of alkaline earth oxides are quite dependent on the starting material and the pretreatment temperature. Schächter and Pines[1] observed that CaO prepared from $Ca(OH)_2$ by calcining at 900 °C had little activity for the isomerization of 1-hexene, while CaO prepared from $CaCO_3$ by the same way showed a high activity. MgO was also reported to vary its catalytic property with the pretreatment temperature for the isomerization of 1-butene[2,3] and H_2–D_2 exchange reaction.[4]

In this study, two kinds of MgO were prepared from magnesium hydroxide and magnesium carbonate hydroxide by evacuating at various temperatures, and examined for their surface properties and catalytic actions for the isomerization of butenes and the alkylation of phenol with methanol.

Experimental

MgO(I) was obtained from magnesium hydroxide (guaranteed reagent of Kanto Chemical Co.) and MgO(II) from magnesium carbonate hydroxide (guaranteed reagent of Merck Co.) by evacuating at various temperatures. X-Ray diffraction patterns of the powder samples evacuated at different temperatures were recorded at room temperature by using CuK_α as a radiation source in air. Specific surface area was measured by applying BET equation to the adsorption isotherm of nitrogen at −196 °C.

The amount of CO_2 and H_2O evolved upon heating the starting material were measured as follows. The sample was evacuated at 100 °C, heated up to 200 °C and kept at this temperature for 2 h for MgO(I) (1 h for MgO(II)), the evolved gas being trapped by liq. N_2. The amount of gas evolved when the liq. N_2 was replaced by dry ice was taken as the amount of CO_2 and the amount still trapped by dry ice was taken as the amount of H_2O.

IR spectra of CO_2 retaining on MgO were measured by using an *in situ* cell. The sample was evacuated at a certain temperature for 2 h and a spectrum was measured at room temperature. Then, the sample was evacuated at a temperature higher than the previous evacuation temperature and a spectrum was measured again. The spectrum of CO_2 adsorbed on MgO was also measured. A sample was evacuated at 600 °C and exposed to a certain amount of CO_2 after cooling to room temperature.

The isomerization of butenes was carried out at 30 °C in a closed circulation system with a volume of about 1350 ml. In a quartz reactor, 17—25 mg of $Mg(OH)_2$ or 10—122 mg of $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$ was placed and evacuated at various temperatures. The butenes were purified by passing through molecular sieves 4A kept at −78 °C. For analysis of butenes, a 5 m column packed with 30% propylene carbonate on Uniport C was operated at 0 °C.

The alkylation of phenol with methanol was carried out at 500 °C in a flow reactor. The catalyst used for the reaction was pretreated under a nitrogen stream at 530 °C or 650 °C for 3 h. The equimolar mixture of phenol and methanol was passed over the catalyst at contact time of 1.9 g·s·ml^{-1}. The products were trapped at 0 °C and subjected to gas chromatographic analysis. A 2 m column packed with polyethylene glycol 6000 on Celite-545 and thermostated at 100 °C was used.

Results

Upon heating $Mg(OH)_2$ and $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$, the amounts of H_2O and CO_2 evolved are shown in Fig. 1. The evolution of CO_2 from $Mg(OH)_2$ continued over a wide range of the temperature from 200 °C to 700 °C, while the evolution of CO_2 from $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$ occurred sharply around 400 °C. On the other hand, the dehydration of $Mg(OH)_2$ began at 200 °C and almost ended around 400 °C, whereas that of $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$ persisted from 100 to 600 °C. The variations of the specific surface area for MgO(I) and MgO(II) are shown in Fig. 2. Decrease in a surface area was more prominent for MgO(II).

In Fig. 3 are shown the IR spectra of $Mg(OH)_2$ and $4MgCO_3\cdot Mg(OH)_2\cdot 5H_2O$ evacuated at different temperatures. In the case of MgO(I), the pairs of

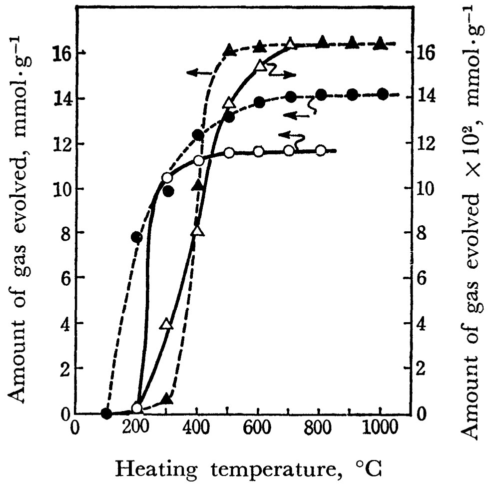

Fig. 1. Evolution of H_2O and CO_2. H_2O (-○-) and CO_2 (-△-) from $Mg(OH)_2$; H_2O (--●--) and CO_2 (--▲--) from $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$.

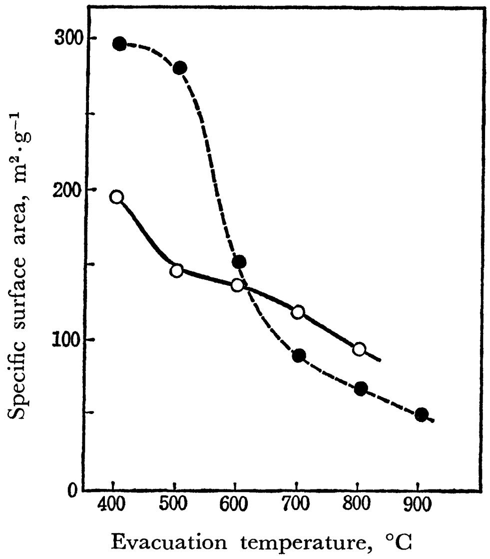

Fig. 2. The variations of specific surface areas of MgO(I) (-○-) and MgO(II) (--●--) with evacuation temperature.

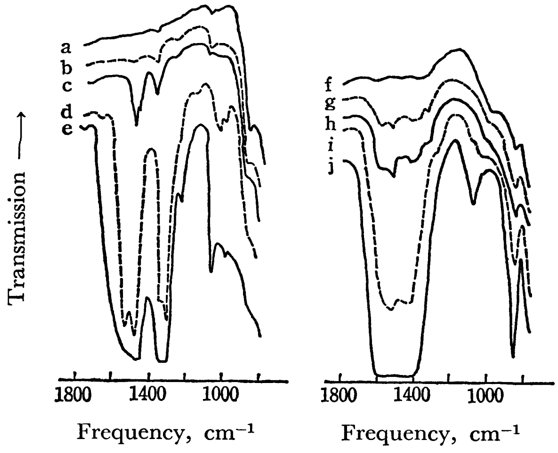

Fig. 3. IR spectra of $Mg(OH)_2$ (left) and $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ (right) after evacuating at a: 700, b: 600, c: 500, d: 400, e: 300, f: 600, g: 500, h: 480, i: 470, j: 460 °C.

the bands at 1520; 1330 cm^{-1} and 1470; 1340 cm^{-1} indicate that two kinds of CO_2 exist. The absorption bands of MgO(II) are rather broad compared with those of MgO(I). Those bands may be superposed bands of several kinds including unidentate CO_2, bidentate CO_2 and CO_3^{2-}.

Spectra of CO_2 adsorbed on MgO(I) were also different from those on MgO(II) as shown in Fig. 4. Spectrum c shows distinct separations of the bands at 1665 ; 1630 cm^{-1} and 1315 ; 1280 cm^{-1}. However, spectrum e obtained when about the same amount of CO_2 as in spectrum c was adsorbed shows indistinctly separated bands around 1650 cm^{-1} and 1300 cm^{-1}. Besides, it shows very broad shoulders around 1550 cm^{-1} and 1400 cm^{-1}.

X-Ray diffraction patterns of both MgO(I) and MgO(II) evacuated at 400—900 °C for 2 h showed only a pattern of MgO. Half width of the peak at $2\theta = 42$ °50′ was about 1 °03′ and 2 °33′ for MgO(I) and MgO(II) evacuated at 400 °C, respectively, while it was about 51′ and 30′ for MgO(I) and MgO(II) evacuated at 900 °C, respectively.

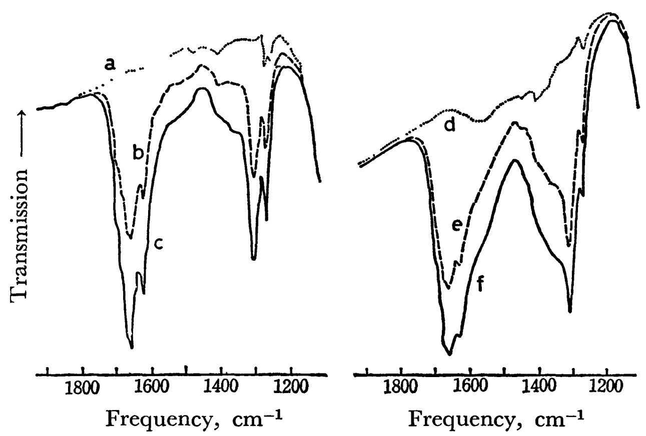

Fig. 4. IR spectra of CO_2 adsorbed on MgO(I) (left) and on MgO(II) (right). a: background of MgO(I), b: 6.5×10^{-5} mol CO_2/g, c: 13.5×10^{-5} mol CO_2/g, d: background of MgO(II), e: 15.0×10^{-5} mol CO_2/g, f: 26.8×10^{-5} mol CO_2/g.

TABLE 1. ALKYLATION OF PHENOL WITH METHANOL OVER MgO

Catalyst		MgO(I)		MgO(II)	
Pretreatment temperature, °C		529	650	533	657
Reaction temperature, °C		498	508	498	505
	phenol	88.1	80.5	72.1	77.2
	o-cresol	10.1	16.9	18.7	15.8
	m,*p*-cresol	0.2	0.4	5.3	4.6
% Each	2,6-xylenol	0.9	1.8	1.2	0.8
Product	2,4-xylenol	0	0.4	2.0	1.3
	2,4,6-trimethyl-phenol	0	0	0.3	0
	anisole	0	0	0.4	0.3
Activity, %·g^{-1}		11.5	18.9	26.9	22.0
ortho-Selectivity[a]		0.98	0.96	0.73	0.74

a) The ratio of (*o*-cresol+2,6-xylenol)/(*o*-cresol+*m*,*p*-cresol+2,6-xylenol+2,4-xylenol).

The results of the alkylation of phenol with methanol are listed in Table 1. MgO(I) was less active than MgO(II). However, the *ortho*-selectivity was more than 96% for MgO(I), while it was about 75% for MgO(II).

For the isomerization of 1-butene, the variations of the activity and the selectivity with evacuation temperature were substantially the same for two kinds of MgO as shown in Fig. 5. The maxima of the activity were observed when evacuated at 600 °C for two MgO. The ratio of *cis*-2-butene to *trans*-2-butene decreased to about 1—2 by raising the evacuation temperature to 600 °C and increased again to about 4—6 by evacuating at higher temperature.

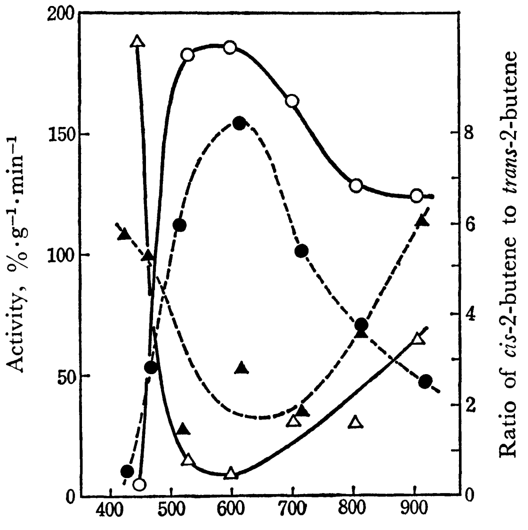

Fig. 5. Activity and selectivity for the isomerization of 1-butene. Activity (-O-) and selectivity (-△-) of MgO(I). Activity (--●--) and selectivity (--▲--) of MgO(II).

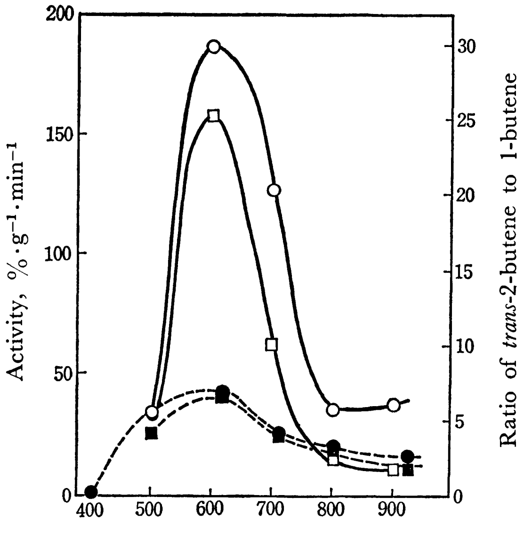

Fig. 6. Activity and selectivity for the isomerization of *cis*-2-butene. Activity (-O-) and selectivity (-□-) of MgO(I). Activity (--●--) and selectivity (--■--) of MgO(II).

Although the shapes of the change in the activity and the selectivity with evacuation temperature were about the same for the isomerization of *cis*-2-butene, the values of the activity and the selectivity were different for two MgO as shown in Fig. 6. Both the activity and the selectivity of MgO(I) at the maximum values were four times as high as those of MgO(II).

Discussion

The surface properties of two kinds of MgO which were prepared from different starting materials were not the same. Broad IR bands of adsorbed CO_2 on MgO(II) suggest that the surface structure of MgO(II) deviates from regularly ordered MgO surface and consists of several different sites for CO_2 adsorption. Rather sharp IR bands of CO_2 on MgO(I) indicates that the surface structure of MgO(I) is ordered much regularly than that of MgO(II). Since spectra of $Mg(OH)_2$ and $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ evacuated at different temperatures (Fig. 3) shows not only CO_2 on the surface but also CO_2 in the bulk, superposed bands of several kinds of CO_2 observed in MgO(II) indicate that the bulk structure of MgO(II) is also less regularly ordered than that of MgO(I). Since an irregularly ordered structure is not so stable as a regularly ordered structure, a remarkable decrease in the surface area of MgO(II) with a rise of the pretreatment temperature also suggests that MgO(II) is less regularly ordered than MgO(I).

For the alkylation of phenol with methanol, the difference between two MgO was observed in the *ortho*-selectivity. The *ortho*-selectivity was reported to be governed by the adsorption state of phenol.[5] If phenol is adsorbed in such a state that the *para* position is far from the surface, high *ortho*-selectivity is expected. Parallel adsorption of benzene ring to the surface, on the contrary, makes it easy to be alkylated at *meta* or *para* position. Since MgO(II) is considered to have several different kinds of sites, some of them might adsorb phenol in parallel, and produce *m*-, *p*-cresol and 2,4-xylenol.

These differences between MgO(I) and MgO(II), however, did not reflect on the catalytic action for the isomerization of 1-butene. As discussed in the previous paper on MgO(I),[3] the active sites for the formation of *cis*-2-butene appear by removing the carbonate having infrared absorption bands at 1520 and 1330 cm^{-1} and those for the formation of *trans*-2-butene by removing the carbonate having absorption bands at 1470 and 1340 cm^{-1}. Although the pursuit of the kind of CO_2 relevant to activity was not successful because of the existence of several kinds of CO_2 on MgO(II), a coincidence of the variation of the activity and the selectivity with evacuation temperature for two MgO suggests that the active sites of MgO(II) for the isomerization of 1-butene are generated by the same manner as those of MgO(I).

For the isomerization of *cis*-2-butene, the activity and the selectivity changed with evacuation temperature in a similar way for two MgO. The temperature at which the activity increased roughly coincided with the temperature at which CO_2 evolved. As the variation of the activity is parallel to that of selectivity, the variation of the activity would represent the variation of the rate of the formation of *trans*-2-butene, while the rates of the formation of 1-butene are almost constant. Thus, the active sites for the formation of *trans*-2-butene from *cis*-2-butene are also considered to be generated by the evolution of CO_2. The values of the activity and the selectivity of MgO(I), however, were four times higher than those of MgO(II). The reason for this is still uncertain.

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