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Basic Properties of MgO Doped with Alkaline Metal Compounds

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Synopsis Basic properties of MgO doped with NaOH, KOH, and Li_2CO_3 which was calcined at 550, 700, and 900 °C in air were examined. The basicity of the catalysts was determined from the irreversible amount of adsorption of phenol and BF_3, followed by evacuation at room temperature (for both adsorbates), 100, 200, and 300 °C (for phenol) after adsorption at room temperature. A good correlation was observed between the amount of phenol remained after evacuation at higher temperature than 200 °C and that of BF_3. By doping of 1 wt% of alkali metal compounds in MgO the isomerization activity of 1-butene was enhanced, but by 10 wt% the activity remarkably decreased.

The studies on the addition effects of sodium hydroxide on the physicochemical properties of MgO were reported by Malinowski *et al.*[1] in which any change in the acidic or basic strength of MgO was not found. In the literature[2] the basicity of the catalysts containing 0 to 0.82 mmol Na^+/g MgO were examined. However, there is no report on the studies of the catalysts containing more than 0.82 mmol and other alkali metal compounds except NaOH. In this study the effect of the addition of KOH, Li_2CO_3, and also NaOH on the basicity of MgO was examined in connection with 1-butene isomerization and, in part, reexamined the results of Malinowski *et al.*[2]

Experimental

Catalysts Preparation. Magnesium hydroxide was first prepared by precipitating with aqueous ammonia (6 mol dm^{-3}) from the saturated aqueous solution of magnesium nitrate. Thus prepared $Mg(OH)_2$ was impregnated into the aqueous solution of NaOH, KOH, and Li_2CO_3 of different concentration which was arranged to be 1 and 10 wt% as M^+ per MgO (M^+ is alkali metal ion) after calcination and then evaporated to dryness on the water bath. The dry $Mg(OH)_2$ doped with the each alkali metal compound (abbreviated simply as dopant) was arranged to the granule of 20 to 60 mesh, which were calcined at 550, 700, and 900 °C for 3 h in air. Magnesium oxide not doped with the dopants was prepared by the calcination of $Mg(OH)_2$ at 550, 700, and 900 °C for 20 h in air.

Measurement of Basicity. Basicity was determined from the irreversible amount of adsorption of phenol or BF_3 according to the spring balance method, *i.e.*, after the adsorption of phenol or BF_3 was attained to equilibrium at room temperature, the sample in the quartz basket was evacuated at room temperature (for both adsorbates) and at 100, 200, and 300 °C (for phenol) until the change of the reading of the quartz spring balance ceased. The strength of the basicity was qualitatively examined with the color change of indicators.[2]

Isomerization of 1-Butene. The isomerization of 1-butene was carried out at 0 °C in a closed vessel (dead volume=*ca.* 180 cm^3) equipped with a circulation system. The reaction products were analyzed by gas chromatography on a column of VZ-7 (4 m) at 0 °C.

Results and Discussion

The irreversible amounts of adsorption of phenol and BF_3, surface area, and basic strength of various samples are shown in Table 1. The adsorbed amounts of phenol decreased as the evacuation temperature of the adsorbed samples increased. The molecular sizes of both phenol and BF_3 were calculated to be 8.24×10^{-20} and 9.62×10^{-20} m^2, from the excluded volumes of the van der Waals equation estimated from the critical points. From the sizes and the adsorbed amounts of each adsorbate the adsorption of phenol can be calculated to be more than monolayer (for instance, 1.27 and 2.7 molecular layer on MgO–KOH (10) treated at 550 °C (evacuated at r.t.) and 900 °C (at 100 °C), respectively) and, on the other hand, BF_3 adsorbed less than monolayer. By the evacuation at higher temperature than 200 °C, the adsorbed amount of phenol was reduced to less than monolayer. At the temperature of lower than 100 °C phenol of physical adsorption seems to be still remained on the surface. Tanabe[3] reports that phenol adsorbs not only on the basic site but also on the acidic one, indicating that phenol is not necessarily suitable for the measurement of basicity. As shown in Fig. 1, however, a good correlation between the basicity obtained from the adsorption of BF_3 and that from phenol evacuated at 200 and 300 °C was obtained. The measurement of basicity by BF_3 adsorption is also reported by Niiyama and Echigoya.[4] Accordingly, it is possible to measure the basicity by phenol adsorption, if the evacuation treatment at 200 or 300 °C, is followed after the adsorption.

The surface areas of MgO–alkali metal system decrease as increasing the content of the dopants, indicating that they exert the shrinking effect on the surface by any kind of interaction with MgO. As shown in the case of Al_2O_3–$NaNO_3$ system,[5] the dopants will also interact with surface OH groups MgO, causing the decrease of the surface area. This effect was also found in other alkali compounds except those used in this study.[6] In doping of 10 wt% the strength of the basicity decreased, which would be difficult to ascribe to the interaction of the dopants with the OH groups on the surface. The OH groups on MgO will be of weak basic sites as those on CaO.[7] Therefore the dopants will interact with or block over Lewis base site on MgO, resulting to the reduction of the basic strength.

The results of the isomerization of 1-butene over the catalysts doped with the alkali compounds followed with calcination at 550°C are shown in Fig. 2. By doping of 1 wt% of the dopants the isomerization activity was enhanced, but the doping to 10 wt% caused the remarkable decrease of the activity. As shown in Fig. 2 the activity of the catalyst doped with Li_2CO_3 by 1 wt% was the highest, which might be due to both the higher surface area and suitable basicity produced by the interaction with MgO and Li_2CO_3.

TABLE 1. RESULTS OF BASICITY MEASUREMENTS AND SURFACE AREA

Catalyst	Temp[a) °C	Adsorbed amount of phenol (mmol/g)				Adsorbed amount of BF_3 (mmol/g)	Surface area (m^2/g)	Basic strength (H_-)
		r.t.[b,c)	100[c)	200[c)	300[c)			
MgO-NaOH (1)	550	1.11	0.700	0.548	0.479	1.58	131	35
	700	0.494	0.400	0.303	0.281	0.759	61	35
	900	0.269	0.231	0.179	0.142	0.451	30	35
MgO-NaOH (10)	550	1.34	0.688	0.501	0.347	1.36	78	27
	700	0.483	0.243	0.167	0.142	0.449	36	15.0
	900	0.105	0.080	0.069	0.036	—	4.6	15.0
MgO-KOH (1)	550	0.983	0.619	0.492	0.442	1.23	105	27
	700	0.403	0.290	0.213	0.199	0.589	41	22.3
MgO-KOH (10)	550	1.40	0.557	0.375	0.328	0.907	56	22.3
	700	1.10	0.438	0.307	0.212	0.535	26	17.2
	900	0.226	0.191	0.188	0.156	—	3.5	17.2
$MgO-Li_2CO_3$ (1)	550	1.19	0.371	0.504	0.474	1.02	144	35
$MgO-Li_2CO_3$ (10)	550	1.12	0.810	0.534	0.484	1.15	109	27
MgO	500	1.19	0.792	0.653	0.568	1.79	188	27
	700	0.602	0.418	0.373	0.313	1.06	93	27
	900	0.431	0.344	0.269	0.215	0.580	47	27

a) Treatment temperature. b) Room temperature. c) Evacuation temperature (°C) after adsorption. The values of parenthesis in catalyst column indicate the doped amount (wt.%) of alkali metal.

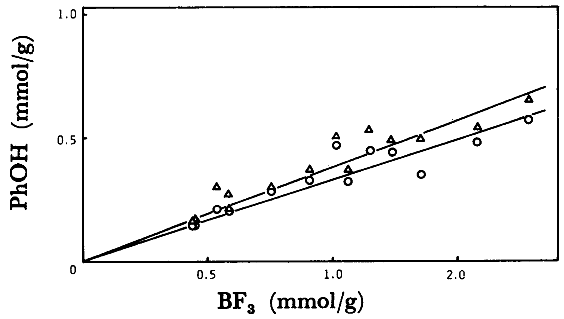

Fig. 1. The relationship between the irreversible amounts of adsorption of phenol and BF_3.
△: Evacuation at 200 °C, ○: at 300 °C.
Each points in the figure were obtained from the results of Table 1.

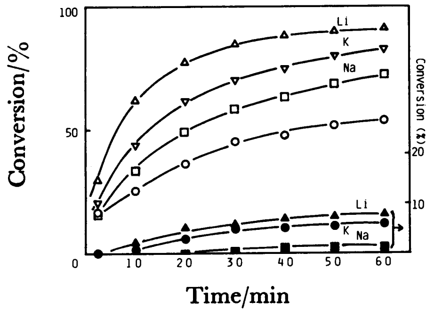

Fig. 2. Conversion *vs.* reaction time plot in 1-butene isomerization.
Open symbols 1 wt% doping.
Closed symbols 10 wt% doping.
○: no doping.

TABLE 2. INITIAL *cis* TO *trans* RATIO IN 1-BUTENE ISOMERIZATION

Catalyst[a)	*cis/trans*
MgO-NaOH (1)	5.7
MgO-NaOH (10)	10.5
MgO-KOH (1)	5.7
MgO-KOH (10)	13.9
$MgO-Li_2CO_3$ (1)	5.8
$MgO-Li_2CO_3$ (10)	7.4
MgO	6.8

a) All catalysts were calcined at 550 °C for 3 h in air except MgO.

As Li_2CO_3 can be decomposed releasing CO_2 at lower temperature (618 °C) than the decomposition temperature of NaOH and KOH, a parts of Li_2CO_3 may be decomposed with the treatment at 550 °C, by which the suitable active sites may be formed. Anyway, by the doping of 1 wt% of the dopants the active sites of the suitable basic strength of H_-=22.3 and 27 for the isomerization[6) will be increased. Deactivation by the addition of 10 wt% of dopants may be ascribed to the considerable decrease in the surface area of the catalysts except the case of $MgO-Li_2CO_3$ and in the sites related with the suitable basic strength. The ratios of cis to trans isomers at the initial stage of the isomerization are shown in Table 2. The ratios exhibited the characteristic values[8) for the basic catalysts, but the correlation between the ratios and basicity including the basic strength could not be found, indicating that it is impossible to evaluate the basic strength of the catalysts from the ratios.

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