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ENHANCEMENT OF SURFACE BASE PROPERTY OF MAGNESIUM OXIDE BY THE COMBINATION OF METAL ION

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Surface base property of magnesium oxide can be modified by the addition of metal ion. The addition of metal ion with larger ionic radius than Mg^{2+} causes the increase of the amount of surface base site, whereas the addition of metal ion with smaller ionic radius than Mg^{2+} shows not to be effective.

We recently reported a widely applicable base-catalyzed synthetic process of α,β-unsaturated compounds.[1] This process involves that the saturated ketones, nitriles and/or esters are converted into corresponding α,β-unsaturated compounds by the addition of methanol as a vinylating agent over solid base catalysts. The most important point in this synthetic process is the utilization of metal ion-containing magnesium oxide as a solid base catalyst for high conversion and high selectivity, and thus we can expect that these improvements in catalytic properties by the combination of metal ion are due to the enhancement of surface base property. For check of this expectation, we measured the surface basicity of the metal ion-containing MgO by CO_2 adsorption and found novel phenomena that the amount of surface base site drastically changed depending on the ionic radius of added metal ions.

The amount of surface base was estimated for various metal ion-containing magnesium oxide catalysts, M-MgO [M = Al(III), Cr(III), Fe(III), Ni(II), Cu(II), Mn (II), Cd(II)], from their adsorption capacity of CO_2. Preparation of catalyst was reported in the previous paper.[1] Adsorption capacity of CO_2 was determined by temperature-programmed desorption method using flow system equipped with mass spectrometer (20 °C/min). TPD profile of CO_2 were recorded after CO_2 adsorption

at ambient temperature on the catalyst pretreated at 600 °C for 2 h in N_2 stream.

Table 1 shows the surface area for each catalyst, the total amount of surface base per gram or per unit surface area, and the fraction of the amount of surface base against that of total lattice oxide ions on the surface. The desorption of CO_2 began at near 50 °C and substantially ceased at about pretreatment temperature for every catalyst. Obtained TPD spectrum patterns did not appreciably change for each catalyst, indicating that no substantial change occurred in surface basicity of MgO by the combination of metal ion. On the other hand, the adsorption capacity of CO_2 for each catalyst was found to fairly depend on the kind of added metal ion.

Table 1. Amount of surface base on various metal ion-containing MgO

Catalyst (3 wt%)	Surface area $m^2 \cdot g^{-1}$	Amount of surface base(adsorbed CO_2) 10^{-4}mol·g^{-1}	Amount of surface base(adsorbed CO_2) 10^{-6}mol·m^{-2}	Fraction[a] %
MgO	11	0.2	1.9	10.2
Al-MgO	106	0.3	0.2	1.3
Fe-MgO	103	2.1	2.0	10.7
Cr-MgO	105	2.1	2.0	10.7
Cd-MgO	143	4.5	3.1	16.6
Mn-MgO	168	5.8	3.5	18.7
Ni-MgO	143	11.4	8.0	42.8
Cu-MgO	124	13.6	11.0	58.8

a) Calculated by assuming that the amount of total lattice oxide ion per unit surface area is 1.87 x 10^{-5}mol for every catalyst.

From the comparison of the amount of surface base site per unit surface area for each catalyst, it is revealed that the addition of Cu(II) ion and/or Ni(II) ion showed the pronounced effect on enhancing the amount of surface base. The amounts of surface base on these catalysts were 4-5 times as high as that on MgO and were corresponding to about 50% of total lattice oxide ion on the surface. The same trend was also observed for the Cd(II) ion- and/or Mn(II) ion-containing MgO catalyst but was not so remarkable as on Cu ion- or Ni ion-containing one. The addition of Fe(III) ion or Cr(III) ion has no effect on the surface basicity. In contrast to above phenomena, the amount of surface base was drastically decreased by the addition of Al(III) ion.[2)]

The amount of surface base was plotted against the ionic radius of added metal ion in Fig. 1. MgO has a non-directional simple ionic crystal with NaCl

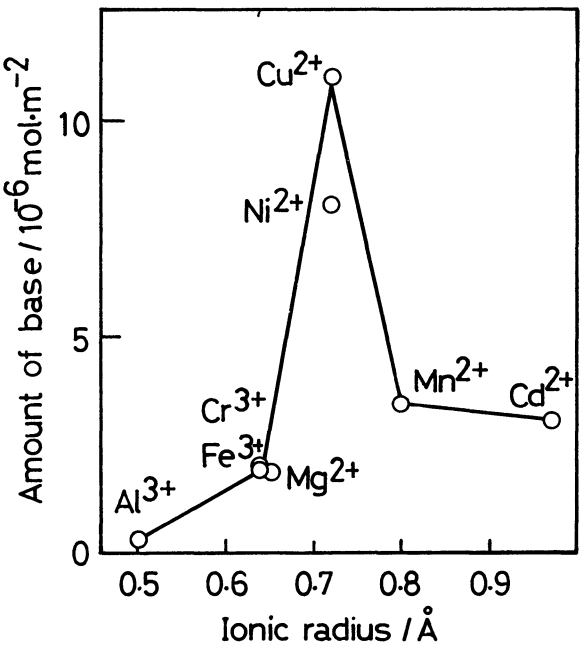

Fig. 1. Relationship between the amount of surface base of metal ion-containing MgO and the ionic radius of added metal ion.

structure and both coordination numbers of Mg^{2+} and O^{2-} ion are 6. The values of ionic radius in Fig. 1 are those for the metal ion with coordination number of 6,[3] by considering that the introduced metal ion into the surface lattice of MgO may settle down into the same circumstance as Mg^{2+}. The charges of metal ion are based on the starting materials in preparation procedure of catalyst. For Fe-MgO and Cr-MgO catalyst, the charges of Fe and Cr were confirmed to be 3+ by ESR measurement and not to change after the heat treatment.

As can be easily seen in Fig. 1, the amount of surface base drastically increases by the addition of metal ion with slightly larger ionic radius than Mg^{2+}, whereas the amount of base decreases when the metal ion with smaller ionic radius than Mg^{2+} was added to MgO. The addition of metal ion with far larger ionic radius such as Mn^{2+} and/or Cd^{2+} is revealed not to be appreciably effective for the enhancement of surface basicity.

The obtained relation between the amount of surface base of metal ion-containing MgO and the ionic radius of added metal ion is explained as follows. When metal ion of which radius is larger than that of Mg^{2+} is incorporated into the MgO lattice, a distortion occurs in the lattice which surrounds the added metal ion. The distortion may result in the expansion of Mg-O bond length and localization of electron on oxygen atom. Consequently, solid base property may appear or increase. The result that the addition of metal ion with far larger ionic radius showed small effect (Fig. 1) may be ascribed to that the metal ion is not able to be incorporated into the lattice because of its larger ionic radius than Mg^{2+}.

To make sure the enhancement of surface basicity of MgO by the addition of metal ion, catalytic activity of each catalyst for the dehydrogenation of isopropyl alcohol (IPA) as a base catalyzed reaction was investigated. Reaction was carried

out by using pulse reaction techniqe. Reaction conditions and results are shown in Table 2. All catalysts mainly catalyze the acetone formation and the activity order was essentially the same as the base order showed in Table 1. Fe, Cr, or Cd containing catalyst also showed the surface acid property as revealed by production of the small amount of propylene. This result indicates that some added metal ion can exist as a acidic site on the basic surface.

It was already clarified by IR study that the surface base site on alkaline-earth oxide was ascribed to lattice oxide ion, O^{2-},[4] but there are many umbiguous points on the factor to decide its basic property. The above nevel phenomena may prove the importance of structural factor for solid base.

Table 2. Dehydrogenation and dehydration of IPA[a]

Catalyst (3 wt%)	Conversion %	Selectivity /%	
		Acetone	propylene
MgO	2.9	100	-
Al-MgO	2.3	≈100	tr
Fe-MgO	29.3	95.1	4.9
Cr-MgO	30.5	92.4	7.6
Cd-MgO	42.8	98.3	1.7
Mn-MgO	47.9	≈100	tr
Ni-MgO	44.5	100	-
Cu-MgO	81.2	100[b]	-

a) Pulse size: 0.5 μl, reaction temperature: 255 °C, flow rate of nitrogen (carrier): 20 ml/min, catalyst weight: 15 mg, pretreatment: 600 °C for 2 h.
b) Acetone formed partly condensed to give mesityl oxide.

References

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2) The reason for the decrease of the amount of surface base site by combinating aluminum ion is umbiguous at the moment. Reverse result was reported for binary metal oxide, Al-Mg-O. See, S. Miyata, T. Kumura, H. Hattori, and K. Tanabe, Nippon Kagaku Zasshi, 92, 514(1971).
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