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Catalytic Properties of Magnesium Oxides doped with Sodium Compounds

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The physicochemical properties and catalytic activity of MgO doped with sodium compounds that are readily decomposed into sodium or sodium oxides have been examined. By calcination of the MgO doped with such sodium compounds as $NaBH_4$, $NaNH_2$ and $NaNO_3$ at 500 or 700 °C in a flowing inactive gas the basic strength of the MgO increased and the concentration of the basic sites attained a maximum at a loading of 1–3 wt % of sodium. The surface area of the MgO was decreased by the doping of sodium, especially when $NaNO_3$ was the dopant. The cause of the decrease in surface area was ascribable to the sintering effect by sodium on MgO owing to compound formation between MgO and sodium or its compounds. On the other hand, the concentration of one-electron donor centres was a minimum at a loading of *ca.* 2 wt % of sodium, which was inferred as the cause of both the adsorption of sodium on the centres and the migration of sodium on the MgO surface.

The dehydrogenation of cumene proceeds on the basic sites and its activity could be correlated with basic sites with $pK_a > 15.0$.

It has been reported[1] that the catalytic system obtained by the evaporation of metallic sodium on MgO exhibits such extremely strong basicity as $pK_a = 35$, accompanied by the increase of the concentration of both basic and one-electron donating sites. However, there is little described about the dependence of the doping amount on the physicochemical properties of MgO, perhaps because of the technical difficulty in evaporating a definite amount of sodium. We also tried the method of evaporating sodium on MgO and found that it was difficult to achieve homogeneous evaporation of the sodium on MgO when the MgO was a fine powder. Accordingly, it is expected that using sodium compounds that are readily decomposed into metallic sodium at *ca.* 500 °C, similar effects to the evaporating method mentioned in the literature will be obtained. By calcination of a mixture of MgO and sodium compounds tried in this study the relationship between the physicochemical properties and the doping amount of sodium in MgO could be clarified easily. It is also reported[2] that the dehydrogenation of cumene proceeds mainly on one-electron donor centres. However, the results in the literature[2] which led to such conclusions seemed to be rather obscure. In order to check the results in the literature the dehydrogenation of cumene was carried out as a probe reaction.

Experimental

Materials

Three kinds of MgO were obtained as follows: MgO(I) was prepared by calcination of $Mg(OH)_2$ at 550 °C for 20 h in air. The $Mg(OH)_2$ was obtained by precipitation of a saturated aqueous solution of magnesium nitrate with aqueous ammonia. MgO(II) was prepared from commercial $Mg(OH)_2$ (Wako Pure Chemicals) by calcination under the same conditions as MgO(I). MgO(III) was prepared from $Mg(OH)_2$ which was kindly offered from Kohnozima Chemicals. In this case the calcination was carried out in a dry argon flow at 700 °C for 5 h, according to the method described in the literature.[1]

The sodium compounds $NaBH_4$, $NaNH_2$ and $NaNO_3$ were used. Mixtures of MgO(I)–$NaBH_4$ and MgO(II)–$NaNH_2$ were calcined at 700 and 550 °C for 3 h in purified dry Ar flow with a Cu–kieselgur catalyst at 200 °C and molecular sieves and stored in a desiccator. In the case of doping with $NaNO_3$, $Mg(OH)_2$ [as the starting material of MgO(III)] was impregnated with an aqueous solution of $NaNO_3$, dried at 110 °C and then calcined at 700 °C for 5 h in a dry Ar flow. The purity of all reagents for the preparation of MgO was $>99.9\%$.

Measurements of Basicity and One-electron Donor Centres

The measurement of basicity was performed by two methods: (i) by titration with benzoic acid in benzene according to the method of ref. (3) and (ii) by gravimetric measurement using a spring balance, *i.e.* the basicity was determined from the amount of irreversible adsorption of phenol at 200 °C. The concentration of one-electron donor centres was determined by e.s.r. spectroscopy at room temperature by determining the tetracyanoethylene radical formed on the catalyst surface.[1]

Surface Area and Pore Distribution

Surface area was determined from the adsorption of nitrogen at -196 °C by the B.E.T. method. The pore distribution and pore volume were also determined by nitrogen adsorption at -196 °C according to Inkleys's method.[4]

Dehydrogenation of Cumene

The dehydrogenation of cumene was carried out in a quartz flow reactor (i.d. = 18 mm, length = 30 cm). The feed rate of cumene was 34.1 mmol h^{-1}, accompanied by 30 cm^3 min^{-1} Ar, and the reaction was carried out at temperatures between 500 and 550 °C, using 2 g of catalyst. The catalyst was treated at 500 °C for 2 h in Ar before the reaction. The reaction products were collected every 30 min, weighed and analysed by gas chromatography, using acetone as the internal standard. A 4.5 m stainless-steel column packed with PEG 20 M (5%) supported on Celite 545 was operated at 100 °C, using He as the carrier gas.

Results and Discussion

Surface Area and Basicity

The surface areas and basicities of various magnesium oxides doped with sodium compounds are listed in table 1. The surface area of MgO decreased with the progressive increase of the loading of sodium, especially in the case of MgO(III)–$NaNO_3$. Doping with $NaBH_4$ and $NaNH_2$ did not result in such a drastic decrease of the surface area. The cause may be ascribed to gas evolution accompanied by the decomposition of $NaBH_4$ and $NaNH_2$ during the calcination process. Since the decrease of the surface area is considered to be due to filling the pores of the MgO with sodium or sodium compounds formed by the thermal decomposition of the original sodium compounds, measurements of the pore distribution were made.

The pore distribution was calculated using the full N_2 adsorption isotherm on MgO(III) typical for all systems (see fig. 1). As shown in fig. 2, the number of pores of diameter ≈200 Å (and 20–50 Å) in MgO was decreased markedly by the doping of sodium nitrate.

Table 1. Surface properties of MgO doped with sodium compounds

catalyst	Na compound	doping amount Na (%)	surface area/m^2 g^{-1}	basicity /mmol g^{-1}
MgO(I)	$NaBH_4$	0	103	0.270[a]
		1	84.1	0.289
		2	81.2	0.309
		5	78.4	0.162
MgO(II)	$NaNH_2$	0	34.8	0.155[a]
		0.8	32.2	0.171
		2	25.9	0.121
		5	10.1	0.090
		8	5.0	0.121
		10	3.8	0.029
MgO(III)	$NaNO_3$	0	49.9	0.169[b]
		0.8	17.9	0.186
		2.4	11.0	0.424
		3.6	5.0	0.530
		7.4	1.5	1.041

[a] Phenol was adsorbed at room temperature and then evacuated at 200 °C. [b] Basicity was measured by titration with benzoic acid in benzene solution: indicator (phenolphthalein, $pK_a = 9.3$).

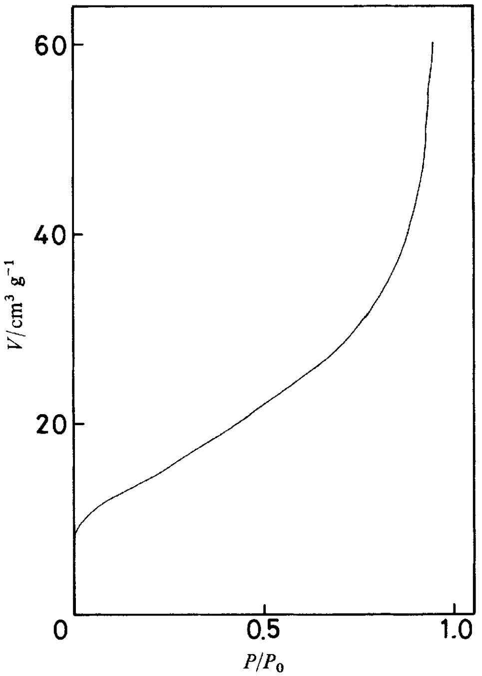

Fig. 1. Adsorption isotherm of N_2 at −196 °C for the MgO(III) catalyst. The adsorbed amount of $N_2(V)$ *vs.* the relative equilibrium adsorption pressure (P/P_0) of nitrogen to its saturated vapour pressure (P_0).

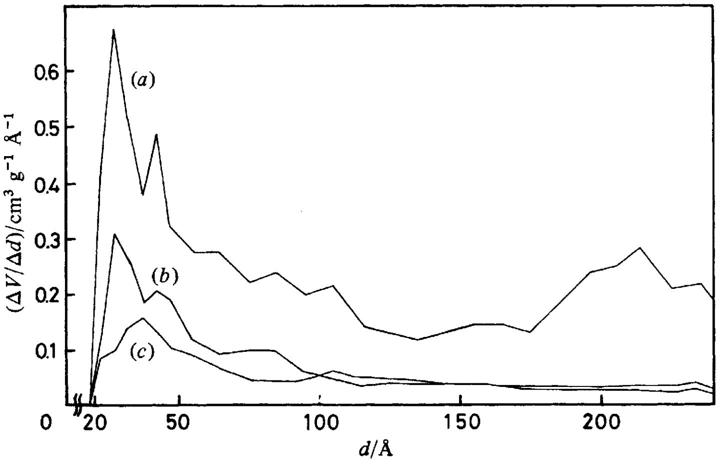

Fig. 2. Pore distribution of MgO(III)–$NaNO_3$ catalyst (pore volume per $cm^3\ g^{-1}$ in parentheses): (*a*) MgO (0.0947); (*b*) Na, 0.8 wt % (0.0307); (*c*) Na, 2.4 wt % (0.0196).

The pore volumes of the MgO(III) and MgO(III)–$NaNO_3$ catalysts are listed in fig. 2. The pore distribution below 20 Å could not be obtained by calculation, since the surface areas of MgO doped with sodium compounds were small and a factor of Inkley's equation showed negative values in this region. If one assumes that non-decomposed $NaNO_3$ or Na fills the pores to reduce the pore volume, the decreased values of the pore volume from doping with 0.8 and 2.4 wt % $NaNO_3$ are rather large in comparison with the volume of $NaNO_3$ doped or of $NaNO_2$, which is the half-decomposed product of $NaNO_3$ (the decomposition of $NaNO_3$ will be discussed later). Blocking of the necks of MgO pores by sodium salts as another cause of decreased surface area may be also considered. However, if this is the case, the drastic decrease of the surface area which occurs in the case of MgO–$NaNO_3$ should also occur in MgO–$NaBH_4$ and MgO–$NaNH_2$. Such a drastic decrease was not detected (table 1). Therefore, pore-neck blocking of MgO is not considered to be an important cause of decreased surface area. Consequently, the decrease of the surface area is likely to result mainly from some sintering effect of $NaNO_3$ or $NaNO_2$ on MgO. The maximum basic strengths of MgO(I) and (II) measured qualitatively by indicators[1, 3] were $pK_a = 22.3$ (diphenylamine indicator) and 17.2 (4-chloro-2-nitroaniline indicator), respectively. After sodium doping the strengths increased to 27 (aniline indicator) and 22.3, respectively. However, basic strengths as high as $pK_a = 35$, as cited in the literature,[1] could not be observed. In the case of MgO(III) the basic strength increased from $pK_a = 15.0$ (2,4-dinitroaniline indicator) to 17.2 after doping with $NaNO_3$. Thus, sodium doping of MgO did not raise the basic strength from a weak degree to a very strong one, for instance from $pK_a = 15.0$ to 27 or 35. It is therefore necessary to produce a very basic MgO initially if one wishes to produce an extremely basic MgO (with $pK_a = 35$).

The basicity attained a maximum with a loading of 1–3 wt % of sodium for the MgO–sodium compound systems [for MgO(III)–$NaNO_3$ $pK_a > 15.0$]. The maximum basicity in MgO(I)–$NaBH_4$ and MgO(II)–$NaNH_2$ catalysts did not agree owing to the different sodium compound and magnesium oxide, respectively. The basicity of MgO showed a marked dependence on the starting materials for the preparation of $Mg(OH)_2$.[3, 5] When $Mg(OH)_2$ was prepared by the precipitation of magnesium nitrate with ammonia solution followed by inadequate washing and calcination in air, the pK_a obtained was no higher than 27.

The number of basic sites of the MgO(I)– and MgO(II)–sodium systems, as shown in

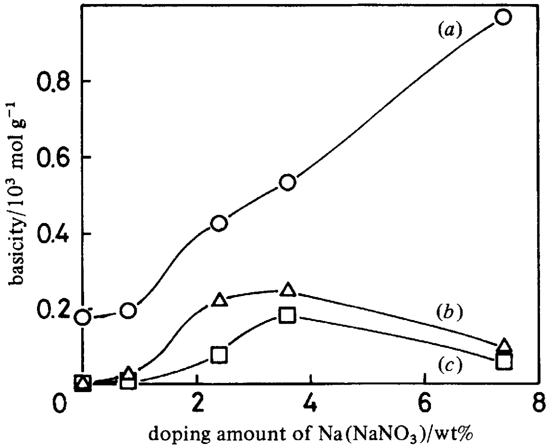

Fig. 3. The relationship between the basicity of MgO(III)–$NaNO_3$ catalyst and the doping amount of $NaNO_3$ as Na. pK_a = (*a*) 9.3; (*b*) 15.0; (*c*) 17.2.

table 1 (determined from the amount of phenol remaining adsorbed after evacuation at 200 °C), can be inferred to correspond to a stronger basicity than pK_a = 15.0, by comparison with the results of fig. 3. The effects of the increase of both the number of basic sites and basicity caused by sodium doping may be due to the inductive effect or electron-donating property of sodium, enhancing the electron density on the oxygens neighbouring MgO which is bound to sodium. However, it is considered that, as a large amount of sodium was doped, it will bind with the basic sites and decrease the basicity.

The pK_a of 9.3 for MgO(III)–$NaNO_3$ catalysts (table 1 and fig. 3) determined from the amount of benzoic acid adsorbed seems to be too large, as seen in the case of 3.6 and 7.4% of Na doped, because the benzoic acid can be estimated to be adsorbed at coverages greater than a monolayer (from the value of the area occupied by the benzoic acid of 3.22×10^{-19} m² per molecule, which is calculated from the density of solid benzoic acid at 25 °C). However, it is rational to consider that the carboxylic group in the benzoic acid combines with the basic site on the MgO. Consequently the calculation should be made with the value of 20×10^{-20} m² as the cross-section of the carboxylic group.[6] In any case the pK_a of 9.3 for 7.4 wt% of sodium doped is unusual. The interaction between benzoic acid and the decomposition products of $NaNO_3$ may cause the high basicity, but this unusual tendency was also found in repeated experiments. The amounts of benzoic acid adsorbed at pK_a 15.0 and 17.2 are suitable as they represent less-than-monolayer coverage. In the case of phenol adsorption it was estimated that phenol of less-than-monolayer coverage was adsorbed when it was outgassed at 200 °C. Therefore, outgassing at 200 °C was adequate, as already clarified.[5]

One-electron Donor Centres

The spin concentration of one-electron donor sites had a minimum at a loading of *ca.* 2 wt% of sodium in both the MgO(II)–$NaNH_2$ and MgO(III)–$NaNO_3$ catalyst systems as shown in fig. 4. The one-electron donor site is a free electron located in an anion vacancy in MgO.[7] Cordischi *et al.*[8, 9] and Garrone *et al.*[10] mentioned that O^{2-} was formed by the adsorption of oxygen on the one-electron donor sites of low coordination on the surface and that a parallel between the one-electron donor activity and Lewis basicity existed. One-electron donor centres which are different in chemical nature may exist on the MgO surface owing to the presence of different electron-acceptor reagents such as

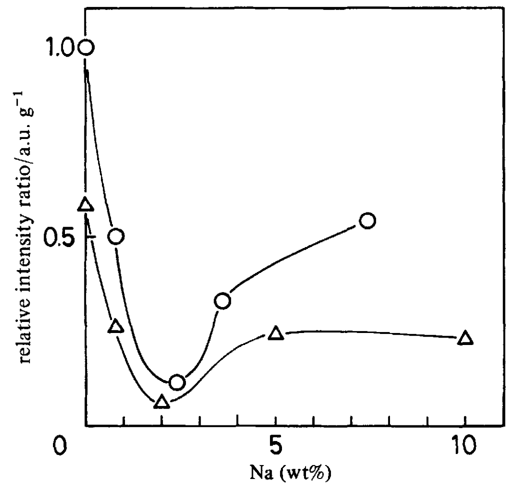

Fig. 4. Relative spin concentration of TCNE radical as a function of the doping amount of Na. ○, MgO–$NaNO_3$; △, MgO–$NaNH_2$.

tetracyanoethylene, nitrobenzene, *m*-dinitrobenzene and oxygen.[1, 2, 9] The different strength of interaction of the one-electron donor centres found by the various reagents will depend on the donating strength of electron.

The relationship between basicity and the one-electron donor centre could not be found in our results. It is very difficult to explain why the concentration of the one-electron donor centre attained a minimum at sodium loading of *ca.* 2 wt %. However, the following may be speculated: when the loading of sodium is low, it selectively adsorbs on the one-electron donor centres, reducing their concentration and simultaneously increasing the electron density of the neighbouring oxygen atoms and leading to an enhancement of the basicity. Increasing the loading of sodium causes migration to the basic sites, leading to a reduction of the basicity and recovery of the one-electron donor sites. Finally, with very high sodium loadings, both the basicity and the number of one-electron donor centres are diminished. It is known that sodium in glass migrates easily within the inner part or from the inner part to the surface when at high temperature or when treated with SO_3.[11] Thus, if sodium migrates in the solid, the abovementioned concentration would be rational.

X-Ray Diffraction and D.T.A.

In the case of high loading of $NaBH_4$, *i.e.* $>5\%$ as Na, very little X-ray diffraction pattern due to the remaining $NaBH_4$ could be detected in the calcination at 500 °C, and none at all at 700 °C. The MgO(II)–$NaNH_2$ catalysts exhibited only the pattern of MgO after calcination at 550 °C; sodium or its compounds as produced by the decomposition of $NaBH_4$ or $NaNH_2$ could not be detected. On the other hand, when the loading of $NaNO_3$ was high, *i.e.* >3.6 wt % as Na, half-decomposed compounds were observed which may be formed by the interaction between MgO and $NaNO_3$ (see fig. 5). For a low loading of $NaNO_3$, only the pattern of MgO could be determined. Unknown peaks may exist, but go undetected owing to their low concentration. The d.t.a. patterns of MgO–$NaNO_3$, $Mg(OH)_2$ and $NaNO_3$ are shown in fig. 6. The broad endothermic peak [indicated by an arrow in fig. 6(*b*)] at *ca.* 500 °C in the MgO–$NaNO_3$ catalyst system, which could not be observed with $Mg(OH)_2$ and $NaNO_3$, indicates the occurrence of an interaction between MgO and $NaNO_3$. Lycourghiotis *et al.*[12] mentioned that $NaNO_3$ interacted with

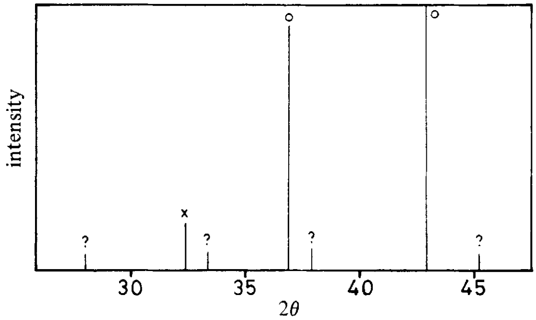

Fig. 5. X-ray diffraction pattern of MgO(III)–$NaNO_3$ (Na, 3.6 wt%) catalyst. ×, $NaNO_2$; question marks indicate the unknown peaks.

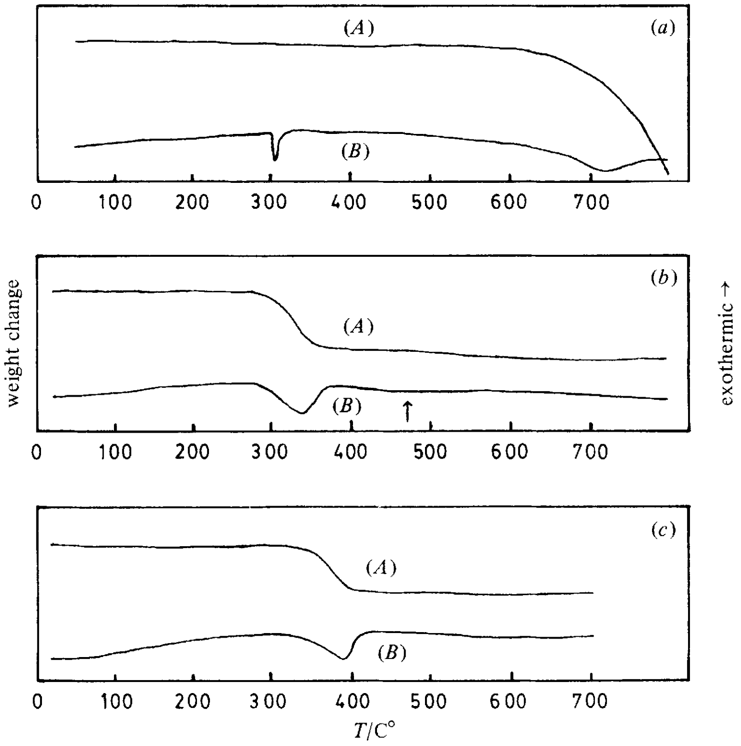

Fig. 6. (A) T.g.a. and (B) d.t.a. of (a) $NaNO_3$, (b) $Mg(OH)_2$–$NaNO_3$ and (c) $Mg(OH)_2$.

Al_2O_3 at *ca.* 600 °C, although they used a different catalyst system from ours. When $NaNO_3$ is mixed with MgO or Al_2O_3, it decomposes at a lower temperature than does $NaNO_3$. If sodium is located in place of magnesium in the MgO lattice the diffraction pattern of MgO will be shifted. However, such a shift of the diffraction peaks could not be detected. Therefore, sodium must combine with the oxygen atom in MgO and not displace Mg in the MgO lattice.

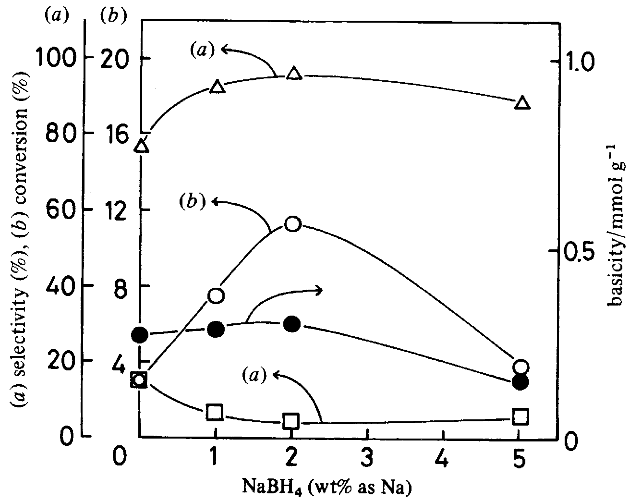

Fig. 7. The relationship between basicity and conversion and selectivity in the dehydrogenation of cumene. MgO(I)–$NaBH_4$ catalyst calcined at 700 °C. (*a*) Selectivity (%), (*b*) conversion (%). △, Selectivity to α-methylstyrene; □, selectivity to ethylbenzene. Reaction temperature = 500 °C. Basicity was measured by the amount of irreversible adsorption of phenol at 200 °C.

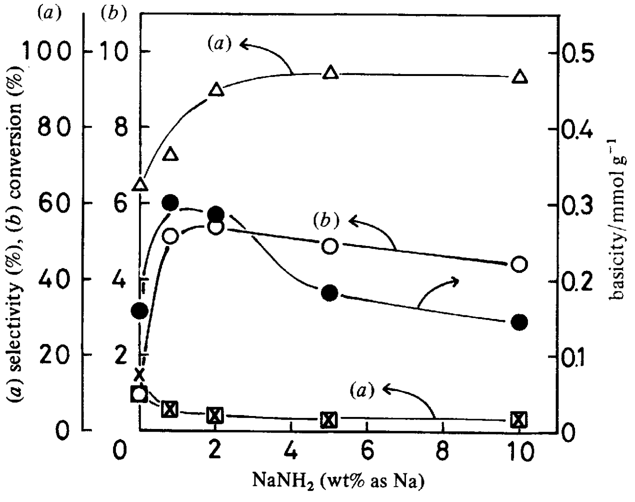

Fig. 8. The relationship between basicity, conversion and selectivity. MgO(II)–$NaNH_2$ catalyst calcined at 550 °C. ×, Styrene, other symbols are the same as those in fig. 7. Reaction temperature = 500 °C.

Dehydrogenation of Cumene

The conversion of cumene (per 2 g catalyst) increased with the reaction time and attained a stationary state after 1.5–2 h. The results of dehydrogenation of cumene at 500, 530 and 550 °C over the MgO–$NaBH_4$, –$NaNH_2$ and –$NaNO_3$ catalysts are shown in fig. 7–10. The conversion of cumene and the selectivity to α-methylstyrene were maximum at a loading of *ca.* 1–3 wt % of Na. The enhancement of the activity of the dehydrogenation by the loading of sodium is related to the basic site produced by the interaction of MgO and sodium. Good correlation could be obtained between the

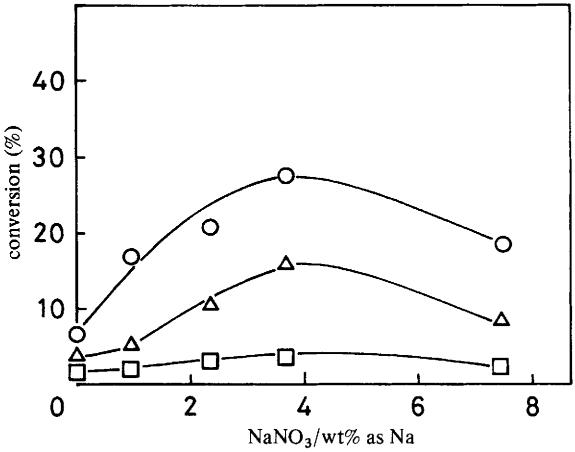

Fig. 9. Cumene conversion *vs.* sodium content of MgO(III)–$NaNO_3$ catalyst at various temperatures: ○, 550; △, 530; □, 500 °C.

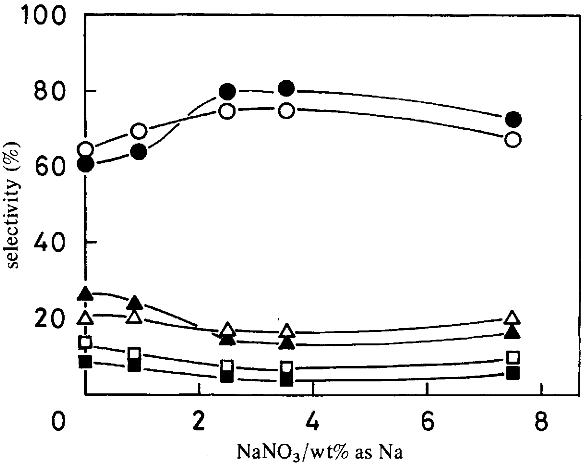

Fig. 10. Selectivity to various products in the cumene dehydrogenation at 530 and 550 °C as a function of the sodium content in MgO(III)–$NaNO_3$ catalyst. ○ and ●, α-methylstyrene; △ and ▲, styrene; □ and ■, ethylbenzene. Open symbols, reaction temperature = 550 °C; closed symbols, reaction temperature = 530 °C.

basicity, conversion and the selectivity to α-methylstyrene as shown in fig. 7–10. This led to the conclusion that dehydrogenation of cumene to α-methylstyrene proceeded on the basic site and not on the one-electron donor site. The correlation was especially good when sites with $pK_a > 15.0$ were involved. The selectivity by-products such as styrene and ethylbenzene seems to be related with the one-electron donor property, although conversion to the by-products was very small. Small amounts of methane and hydrogen were produced in the dehydrogenation. Methane is produced by the combination of hydrogen and methyl radicals formed by the decomposition of cumene.

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Paper 5/809; *Received* 14*th May*, 1985