Pronounced Catalytic Activity of Magnesium Oxide and Calcium Oxide in Isomerization of Penta-1,4-diene to Penta-1,3-diene

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Summary MgO and CaO showed very high activity for the title isomerization compared with ZnO, TiO_2 or silica–alumina; the ratio of the isomerization activity of penta-1,4-diene to that of but-1-ene was *ca.* 10^7 times higher over the alkaline earth metal oxides than over silica–alumina.

THE catalytic activity of MgO and CaO in the isomerization of butenes was reported to be due to the action of the basic sites.[1] Since penta-1,4-diene has allylic hydrogen atoms which are much more easily abstracted as protons than hydrogen atoms in butenes, the activity of the alkaline earth metal oxides and other oxides has been examined for the isomerization of the diene and compared with the activity for the isomerization of but-1-ene.

Magnesium and calcium oxides were obtained by evacuating their hydroxides at 400 and 280 °C, respectively. Silica–alumina was prepared by the co-precipitation of a mixed solution of ethyl orthosilicate and aluminium isopropoxide, the alumina content being 20 wt. %. TiO_2 was

TABLE. The isomerization of penta-1,4-diene and but-1-ene over oxide catalysts

Catalyst	Specific surface area/m^2 g^{-1}	Reaction temp./°C	Initial rate of isomerization/% min^{-1} g^{-1}		r_1/r_2[a]
			Penta-1,4-diene r_1	But-1-ene r_2	
MgO	40	0	5×10^2	3×10^{-2}	2×10^4
CaO	4·8	0	3×10^3	9×10^{-2}	3×10^4
ZnO	4·9	0	1	9×10^{-3}	1×10^2
SiO_2-Al_2O_3	170	0	3×10^{-2}	2×10	2×10^{-3}
TiO_2	72	0	1×10^{-4}[b]	6×10^{-5}[c]	2

[a] Ratios of initial rates of the isomerization of penta-1,4-diene to those of but-1-ene. [b] Extrapolated from the values at 100 and 120 °C. [c] Extrapolated from the values at 80, 100, and 120 °C.

prepared by the hydrolysis of $TiCl_4$. ZnO was purchased from Wako Junyaku Co. Ltd. These three oxides were calcined at 500 °C in air followed by evacuation at 450 °C before use. Penta-1,4-diene and but-1-ene were dried by passing through a synthetic zeolite Zeolum F-9 at 0 and −78 °C, respectively. The reaction was carried out in a closed circulation system, volume 360 cm^3, the pressure of the olefins being 10 cmHg. The products from penta-1,4-diene were only penta-1,3-dienes and those from but-1-ene were but-2-enes.

The initial rate of the isomerization of penta-1,4-diene was very high over MgO and CaO, but low over silica–alumina and TiO_2, intermediate activity being observed over ZnO (Table). Upon raising the evacuation temperature, MgO and CaO became so active that the reaction rate of the diene could not be measured. Thus, low evacuation temperatures (400 and 280 °C) had to be employed for these two oxides. This caused a very low rate of the isomerization of but-1-ene, as expected from the strong dependence of catalytic activity on evacuation temperature.[1,2] The differences in the ratio (r_1/r_2) of the initial rate of the isomerization of penta-1,4-diene (r_1) to that of but-1-ene (r_2) also varied with the catalyst (Table). This ratio for both MgO and CaO was more than 10^7 times as high as that for silica–alumina. The activities of MgO and CaO were about 10^4 times higher for penta-1,4-diene than for but-1-ene, while the activity for the diene was almost the same as, or $<$ 1/100th of that for the monoene over TiO_2 or silica–alumina. In the homogeneous reaction catalysed by potassium t-butoxide,[3] the ratio was reported to be about 10^5. Thus, the high activity and the high ratio found in the present work strongly support the assumption that the reaction proceeds *via* an allyl anion intermediate and the slowest step is the proton transfer from the allylic hydrogen of the diene to the basic sites on the catalyst.

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