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HYDROGENATION OF OLEFINS CATALYZED BY ALKALINE EARTH METAL OXIDES

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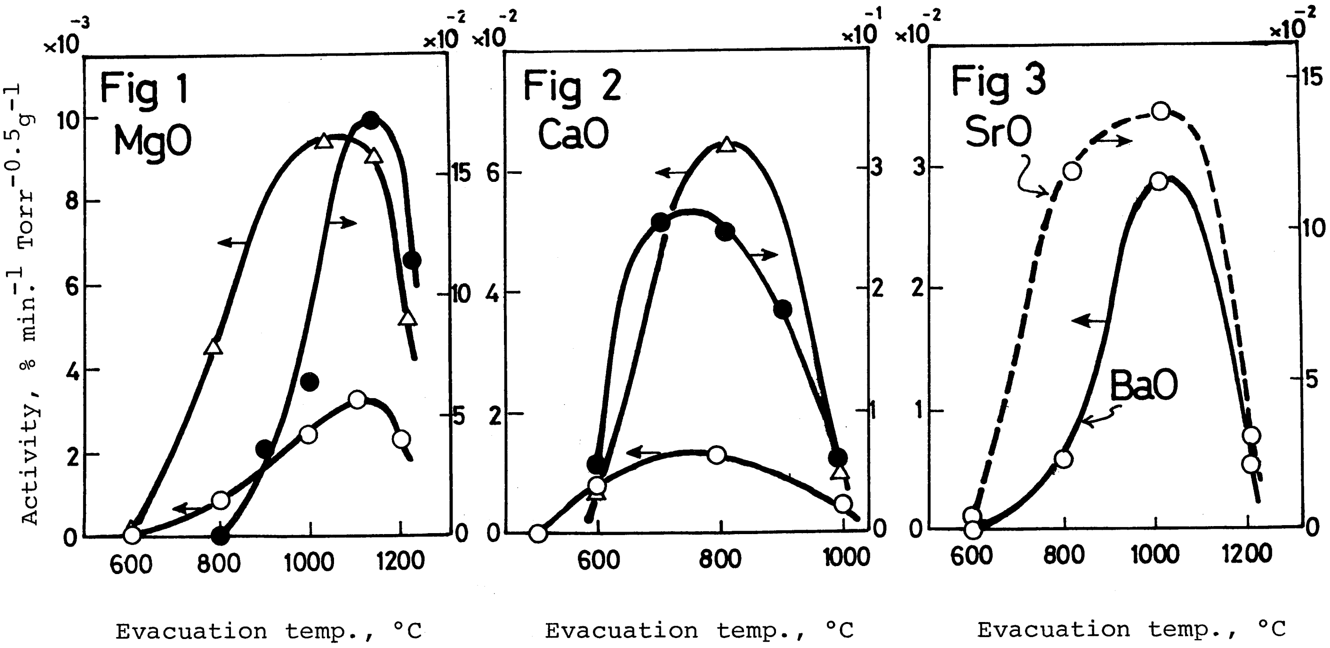
Hydrogenation of olefins was investigated over MgO, CaO, SrO, and BaO at 250°C. The oxides became active on evacuating above 600°C and showed maximum activities when evacuated around 1000°C. The maximum activity increased in the order of $MgO < CaO < BaO < SrO$. The order of the hydrogenation rate was 1-butene $<$ propylene $\ll$ ethylene over MgO and CaO.

In recent years, the catalytic action of alkaline earth metal oxides has been studied with some reactions such as isomerization of olefins,[1-5] polymerization of styrene,[6] esterification of bezaldehyde,[7] and H_2-D_2 exchange reaction.[8] However, few papers have been published on the hydrogenation of olefins over these oxides.[1] In this work, the variations of the activities of MgO, CaO, SrO, and Bao with the evacuation temperature for the hydrogenation of ethylene, propylene, and 1-butene were measured to examine the nature of the active sites.

MgO, CaO, SrO, and BaO were prepared by <u>in situ</u> evacuation of $Mg(OH)_2$ (GR, Kanto Chemical Co.), $Ca(OH)_2$ (GR, Kanto Chemical Co.), $SrCO_3$ (GR, E. Merck Co.), and BaO (GR, E. Merck Co.), respectively. The evacuation was carried out at various temperatures for 2 hr. Olefins and H_2 were purified with molecular sieves 13X kept at -78°C and -195°C, respectively. Premixed gas of olefin (10 Torr) and H_2 (30 Torr) was circulated over the catalysts at 250°C. In poisoning experiments, the catalyst was exposed to a few Torr of ammonia, pyridine, nitrobenzene, or carbon dioxide after cooling to 250°C and evacuated at this temperature prior to the reaction.

The variations of the activity with the evacuation temperature are shown in Figs. 1-3. The catalytic activity increased in the order of $MgO < CaO < BaO < SrO$. With respect to the olefin, the reaction rate increased in the order of 1-butene $<$ propylene $\ll$ ethylene over MgO and CaO. The activities of MgO, CaO, SrO, and BaO reached the maxima for values of evacuation temperatures at 1100°, 800°, 1000°, and 1000°C respectively. These values were considerably higher than those for the isomerization of 1-butene which were 600°,[3] 600°,[3] 800°,[9] and 800°C,[9] respectively and also higher than 500-600°C for the esterification,[7] the polymerization,[6] and the exchange reaction[8] over MgO. Furthermore, MgO did not show any detectable activity for the hydrogenation of olefins when evacuated at 600°C which was the temperature of the maximum activity for the isomerization of 1-butene. Ammonia, pyridine, nitrobenzene, and carbon dioxide completely poisoned the active sites for the hydrogenation, whereas, in the isomerization of 1-butene, ammonia reduced only about a half of the activity.

These results suggest that the hydrogenation of olefins proceeds mainly on the different sites from those for the isomerization, the esterification, the polymerization or the exchange reaction and reveal that a novel kind of active sites appears on the alkaline earth metal oxides by evacuating at higher temperature.



Figs. 1-3. Variation of activity with evacuation temperature.
● ethylene, △ propylene, ○ 1-butene

References

1. Y. Schächter and H. Pines, J. Catal., 11, 147 (1968).
2. I. R. Shannon, C. Kemball, and H. F. Leach, Proc. Inst. Petroleum, London, 46 (1970).
3. H. Hattori, N. Yoshii, and K. Tanabe, Proc. 5th Intern. Congr. Catalysis, Miami Beach, 1972, 10-233 (1973).
4. N. Tani, M. Misono, and Y. Yoneda, Chem. Lett., 1973, 591.
5. M. J. Baird and J. H. Lunsford, J. Catal., 26, 440 (1972).
6. T. Iizuka, H. Hattori, Y. Ohno, J. Sohma, and K. Tanabe, J. Catal., 22, 130 (1971).
7. K. Tanabe and K. Saito, J. Catal., 35, 247 (1974).
8. M. Boudart, A. Deiboulle, E. G. Derouane, V. Indovina, and A. B. Walters, J. Amer. Chem. Soc., 94, 6622 (1972).
9. K. Maruyama and H. Hattori, unpublished data.

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