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SELECTIVE HYDROGENATION OF 1,3-BUTADIENE OVER ALKALINE EARTH METAL OXIDES

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1,3-Butadiene was selectively hydrogenated to butenes without further hydrogenation to butane over MgO, CaO, SrO, and BaO. The oxides showed their maximum activity when evacuated around 800-1000°C, and the maximum activity increased in the order of $BeO \ll BaO < MgO < SrO < CaO$.

Recently, the catalytic actions of alkaline earth metal oxides have been studied with some reactions such as isomerization of olefins,$^{1-5)}$ polymerization of styrene,$^{6)}$ conversion of benzaldehyde into benzyl benzoate,$^{7)}$ and H_2-D_2 exchange reaction.$^{8)}$ On the hydrogenation of unsaturated hydrocarbons, we reported in the preceding paper$^{9)}$ that the active sites for the hydrogenation of olefins on MgO, CaO, SrO, and BaO are different from those for the reactions described above. In the present work, 1,3-butadiene was employed as a reactant to obtain further information about the nature of active sites for the hydrogenation on these alkaline earth metal oxides, and it was found that 1,3-butadiene was selectively hydrogenated to olefins without further hydrogenation to form paraffins.

BeO, MgO, CaO, SrO, and BaO were prepared by in situ evacuation of BeO (Wako Pure Chemical Co.), $Mg(OH)_2$ (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 desired temperatures for 2 hr. 1,3-Butadiene (Takachiho Co.) and H_2 from cylinder were purified with molecular sieves 13X kept at -78°C and -195°C, respectively. Premixed gas of 1,3-butadiene (10 Torr) and H_2 (30 Torr) was circulated over the catalysts at 0°C. Products were analyzed by gas chromatography.

The catalytic activity for the hydrogenation of butadiene was extremely higher than that for the hydrogenation of olefins such as butene, propylene, and ethylene on each oxide; effective hydrogenation of olefins required the reaction temperatures above 250°C, while hydrogenation of butadiene to butenes proceeded readily even at 0°C. A time course of the hydrogenation of butadiene over MgO evacuated at 1100°C is shown in Fig. 1. At initial stage, the product gas consisted of 1-butene, trans-2-butene, and a large amount of cis-2-butene, and the relative amounts of them gradually approached to the thermodynamic equilibrium values. No butane formation occurred even after disappearance of butadine. Except MgO evacuated at 1100°C, all other catalysts produced almost equilibrium mixture of n-butenes from the initial stage, though these catalysts were also completely selective for the butene formation.

Variations of activity with evacuation temperature on each oxide are shown in Fig. 2. BeO did not show any activity. In spite of great difference in catalytic activity between hydrogenation of olefins and that of butadiene, each oxide showed a maximum activity at almost the same evacuation temperatures for both hydrocarbons,[9] these temperatures for 1,3-butadiene are 1100°C for MgO, 800°C for CaO, 800°C for SrO, and 800°C for BaO. Therefore, it is concluded that the active sites for the hydrogenation of 1,3-butadiene are the same as those for the olefins. The maximum activity increased in the order of $BeO \ll BaO < MgO < SrO < CaO$. A great difference in the reactivity between 1,3-butadiene and the olefins as well as a preferential formation of cis-2-butene on MgO evacuated at 1100°C suggests that the hydrogenation of 1,3-butadiene proceeds via a π-allyl carbanion which is expected to be stable on a solid base catalyst. The formation of an equilibrium mixture of the butenes over other catalysts than MgO evacuated at 1100°C is probably caused by a fast isomerization of butenes following the hydrogenation of 1,3-butadiene via a π-allyl carbanion.

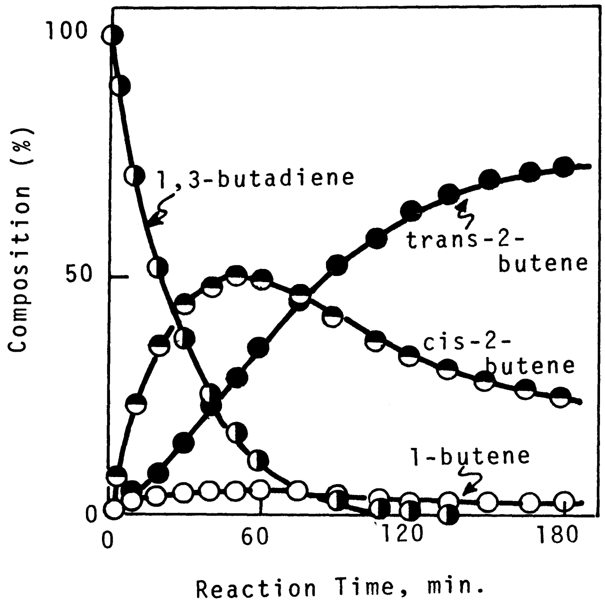

Fig. 1. Hydrogenation of 1,3-butadiene over MgO.

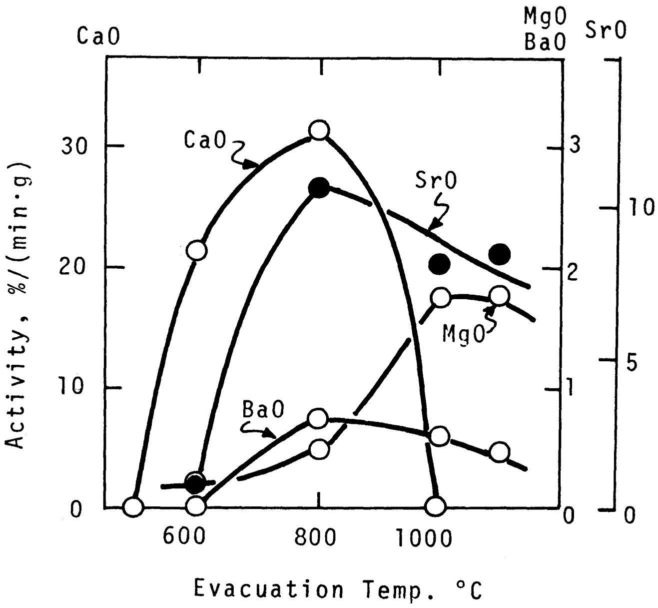

Fig. 2. Variation of activity with evacuation temperature.

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