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# Varieties of MgO Catalysts for 1,3-Butadiene Hydrogenation

The method of preparation is one of the keys to obtaining a solid surface with high catalytic activity and selectivity. It is known (*1*, *2*), as shown in Fig. 1, that MgO prepared by evacuation of $Mg(OH)_2$ above 800°C has a high catalytic activity for selective hydrogenation of 1,3-butadiene to *cis*-2-butene at room temperature. The hydrogenation activity appears by evacuation at ca. 500°C giving 2-butene of the closely equilibrated *trans*/*cis* ratio. These catalytic activities are attributed to the basic characteristics of the MgO surface (*3*); however, a small amount of OH group was still found with ir (*4*) and XPS (*5*) on the MgO surface prepared by evacuation of $Mg(OH)_2$ at 500°C but none of these were detectable when the evacuation temperature was raised to over 800°C.

It has been reported (*6*), on the other hand, that $Mg(OH)_2$ has a hexagonal structure consisting of double layers of OH groups sandwiched in between two Mg layers and MgO crystallites grown by evacuation at 300 ~ 400°C topotaxially with its (111) plane parallel to the basal (0001) plane of $Mg(OH)_2$.

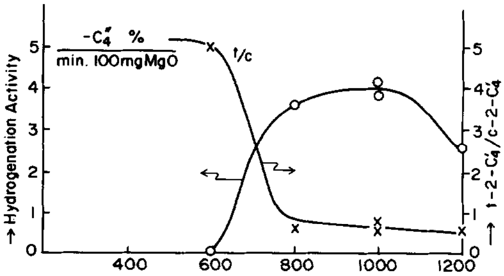

FIG. 1. Hydrogenation of 1,3-butadiene over MgO catalyst prepared by evacuation of $Mg(OH)_2$ at various temperatures.

The recrystallization of MgO to have a stable (001) basal plane was very slow even by evacuation above 800°C, as indicated by the result of electron microscopy, which showed that the original hexagonal plate was unchanged by this heat treatment.

The (001) surface of MgO single crystal (Tatehoh Chem. Ind. Co.) was found to be practically inactive for 1,3-butadiene hydrogenation even though a large number of its fine particles were preevacuated at a temperature between 500 and 1200°C and the reaction temperature was raised to 100°C and kept at this temperature for several hours. This result implies that a surface of MgO other than the (001) plane might be necessary for the catalytic activity. In view of this fact, a variety of MgO samples was examined with respect to 1,3-butadiene hydrogenation.

Hydrogenation of ca. 40 Pa 1,3-butadiene with ca. 140 Pa hydrogen was carried out at room temperature by admitting the mixture into a closed-circulation apparatus of ca. 300 ml volume made of glass, except for a U-tube quartz reaction vessel. The reacting gas at an early stage of the reaction was analyzed by a gas chromatograph equipped with a VZ-7 column and $H_2$ as a carrier at room temperature, with which butene of $10^{-4}$ part of 1,3-butadiene was detectable. The surface area of catalysts was measured by BET method with $N_2$ and/or Kr (*7*) before or after the reactions and the specific activity for the hydrogenation was expediently referred to these surface areas.

Magnesium oxide was prepared by heating, under vacuum, magnesium hydroxide, basic carbonate, and oxalate of chemical purity, and also by mild oxidation of metallic magnesium powder of hexagonal crystallites with water vapor. The $Mg(OH)_2$

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used in the present experiments was made from pieces of MgO single crystal by dissolving it in a hot, aqueous solution of nitric acid, after which it was dried and decomposed at 600°C and finally agitated in hot water and dried at 200°C.

Fine powder of metallic magnesium was obtained by evaporation of Mg pieces of 99.9 purity at ca. 1300°C in an argon atmosphere of 140 ~ 700 Pa. Magnesium thus formed consisted of fine single crystals of hexagonal structure with a (0001) basal plane (*8*). As the argon pressure was increased, larger Mg crystallites formed. A small amount of the powder was supported on quartz wool with *n*-hexane and evacuated in the reaction vessel with a rising temperature to 300°C, where water vapor of a few tens of Pascals was admitted. This amount of water can oxidize 1–2 mg of metallic Mg. The temperature was then raised to 500°C and kept there for 10 min to complete the oxidation of Mg. The sample was evacuated further at 600°C for 10 min and cooled to room temperature. During this preevacuation at 600°C, metallic Mg that was not oxidized was evaporated onto the unheated part of the reaction vessel and the heated part of the vessel and quartz wool became colored a blackish brown, presumably by the formation of magnesium silicate. Catalytic inactivity of metallic Mg and silicate thus formed was ascertained by runs of reaction over a mixture of metallic Mg and quartz wool preevacuated at 600 or 800°C. The surface area of quartz wool was ca. 1.8 $m^2/g$.

The results of the experiments are given in Table 1 and summarized as follows.

1. Magnesium oxide (VII) made by reaction of Mg crystallites with water vapor at 500°C shows a surprisingly high specific activity for selective formation of *cis*-2-butene.

The amount of MgO in this case was estimated from the amount of water vapor used for the oxidation of Mg metal. The structure of MgO thus formed on hexagonal Mg crystallites is unstable as seen from the fact that its catalytic activity decreased remarkably after a brief evacuation at 800°C.

2. Magnesium oxide prepared from oxalate by evacuation at 800°C shows a high activity for *trans*-2-butene formation. The sample obtained from oxalate at lower temperatures appeared to be amorphous and the recrystallization occurred at 1000°C as indicated by the appearance of a diffused halo in its electron diffraction pattern and by a remarkable decrease of its catalytic activity.

3. A MgO sample obtained from a mixture of $Mg(OH)_2$ and a small amount of Mg metal (V) by evacuation at 600°C was colored gray and showed a high catalytic activity for selective formation of *trans*-2-butene and this characteristic was maintained after evacuation even at 1000°C, whereas it disappeared after evacuation at 1200°C.

4. The catalytic behaviors of MgO made from basic magnesium carbonate (III) and from Mg crystallites identical to those (VII) with an excess amount of water vapor were quite similar to that of MgO made from $Mg(OH)_2$.

5. Fine pieces of (001) MgO single crystal (VI) exhibited a specific activity comparable with that of MgO prepared from $Mg(OH)_2$ by mixing it with metallic Mg and heating above 600°C under vacuum.

It has been reported (*8*) that oxygen adsorbed on the (0001) plane of Mg crystal gave a (111) MgO film epitaxially grown on the Mg surface at an elevated temperature. Referring to the catalytic inactivity of the (001) surface of MgO single crystal, facts 1 and 4 mentioned above suggest that the catalytic activity for selective hydrogenation of 1,3-butadiene to *cis*-2-butene is caused by the (111) plane of MgO formed on hexagonal crystallites of $Mg(OH)_2$ or Mg. Fact 2 suggests that a strongly disordered surface of MgO is active for *trans*-2-butene formation; however, it is not clear whether this selectivity for *trans*-2-butene was due to the intrinsic nature of this surface of MgO or a simultaneous rapid isomerization of *cis*-2-butene initially formed.

TABLE 1

Catalytic Activity and Selectivity of Various MgO Samples in 1,3-Butadiene ($C_4''$) Hydrogenation; $C_4'' \sim 40$ and $H_2 \sim 140$ Pa at 20°C for 15–30 min

| Materials | Evac. temp. (°C) | Apparent activity[a] ($C_4''$%/min · 0.1 g MgO) | Selectivity | | Surface area ($m^2/g$) | Specific activity ($C_4''$ molecules/$cm^2$ · sec) |
|---|---|---|---|---|---|---|
| | | | $t$-2-$C_4'$/$c$-2-$C_4'$ | 1-$C_4'$/2-$C_4'$ | | |
| $Mg(OH)_2$, powder (I) | 600 | 0.06 | 5.0 | 0.03 | 254.0 | $0.15 \times 10^9$ |
| | 1000 | 4.1 | 0.6 | 0.06 | | $7.85 \times 10^9$ |
| MgO(001) crystal,[b] 120 mesh (II) | 500 | | | | | |
| | ~1200 | 0.0000 | — | — | 0.6 | 0 |
| Basic Mg carbonate powder (III) | 800 | 0.35 | 1.1 | 0.2 | — | — |
| | 1000 | 0.20 | 0.6 | 0.1 | | |
| Mg oxalate powder (IV) | 800 | 41.1 | 2.0 | 0.04 | 280.0 | $71.4 \times 10^9$ |
| | 1000 | 0.08 | 2.2 | 0.02 | | $0.14 \times 10^9$ |
| $Mg(OH)_2$, powder + Mg metal (V) | 600 | 10.3 | 3.1 | 0.03 | | $43.2 \times 10^9$ |
| | 800 | 9.4 | 1.4 | 0.06 | | $39.4 \times 10^9$ |
| | 1000 | 4.3 | 1.5 | 0.04 | | $18.0 \times 10^9$ |
| | 1200 | 0.2 | 0.6 | 0.15 | 116.2 | $0.84 \times 10^9$ |
| MgO(001) crystal, 120 mesh + Mg metal (VI) | 600 | 0.002 | 1.0 | 0.6 | — | $1.62 \times 10^{9c}$ |
| | 800 | 0.01 | 1.4 | 0.6 | | $8.10 \times 10^9$ |
| Evapd. Mg powder[d] hexagonal, <1 μm) (VII) | 600 | 3.70 | 0.6 | 0.2 | 5.3 | $3.39 \times 10^{11}$ |
| | 800 | 0.31 | 0.6 | 0.1 | | $0.28 \times 10^{11}$ |
| Evapd. Mg powder[e] (hexagonal, >1 μm) (VII) | 600 | 5.24 | 0.5 | 0.1 | — | $4.81 \times 10^{11f}$ |

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[a] Value estimated from the extent of reaction in the earliest sampled gas.

[b] The reaction was carried out at 20 and 100°C for several hours over a catalyst sample of ca. ten times the weight of $Mg(OH)_2$.

[c] The surface area of the catalyst was assumed to be 0.6 $m^2/g$, as was obtained from footnote *b*.

[d] Magnesium was evaporated in argon atmosphere at ca. 140 Pa.

[e] Magnesium was evaporated in argon atmosphere at ca. 420 Pa.

[f] The surface area of the catalyst was assumed to be 5.3 $m^2/g$, as was obtained from footnote *d*.

The catalytic activity of MgO prepared from oxalate and hexagonal Mg crystallites decreased remarkably by heating at high temperatures. Facts 1, 3, and 5 suggest that coordinatively unsaturated Mg ions on the oxygen layer of the (111) MgO surface are active centers for the hydrogenation of 1,3-butadiene, in contrast with the model of Boudart *et al.* (*9*), who have proposed that the active center for $H_2$–$D_2$ equilibration at 78 K on MgO surface preevacuated at a temperature as high as 900°C might be a pair of OH ions and $V_1$ center formed by a defect of the Mg ion at a corner of the (001) MgO crystallite. However, the high activity of the sample obtained from oxalate still suggests a possibility that some defects on the MgO surface may be the active center for the selective formation of *trans*-2-butene.

Furthermore, the fact (fact 3) that *trans*-2-butene was selectively formed over MgO formed from a mixture of $Mg(OH)_2$ and Mg metal preevacuated at 1000°C is interesting when compared with the selective formation of *cis*-2-butene over a sample obtained from $Mg(OH)_2$, preevacuated at 1000°C, alone.

Further investigations, including electron spectroscopy of these active surfaces of MgO, are under way.

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