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Effects of Pressure on the Disproportionation of Olefins over MoO_3-Al_2O_3 and Re_2O_7-Al_2O_3 Catalysts

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The disproportionation of propylene and 1-butene over MoO_3–Al_2O_3 and Re_2O_7–Al_2O_3 catalysts was carried out in order to investigate the effects of reaction pressure in the range from 1.0 to 130 kg/cm^2. The effects of the pressure on the reaction can be identified as two independent of the reaction phase; the catalytic activity increased with the reaction pressure, and the time needed to reach the maximum conversion (T_{max}) as well as the time when the conversion falls to half the maximum value ($\tau_{1/2}$) decreased with the increase in the reaction pressure. It can be concluded that the catalytic activity by the polymers formed over the catalyst falls off rapidly with the increase in the pressure. In both phases, the disproportionation of olefins over the Re_2O_7–Al_2O_3 catalyst exhibits the following features as compared with that over the MoO_3–Al_2O_3 catalyst: (1) a much higher activity at temperatures of 0—140 °C; (2) a much higher selectivity for disproportionation, and (3) a lower apparent activation energy.

The disproportionation of propylene over the MoO_3–Al_2O_3 catalyst shows a high selectivity, but the catalytic activity decreases markedly with the lapse of time.$^{1)}$ Several methods to improve these defects have been studied— *e.g.*, the addition of third materials and solvents.$^{2-4)}$ We reported in the previous papers$^{3,4)}$ that the polymers produced under pressure on MoO_3–Al_2O_3 have high molecular weights.

Hardly studies of the disproportionation of olefins over the Re_2O_7–Al_2O_3 catalyst have been reported. Echigoya and his co-workers observed, however, that the metathesis of isobutene with 2-butene or propylene produces isoamylene in high yields, even at low temperatures.$^{5,6)}$ In the case of disproportionation over the Re_2O_7–Al_2O_3 catalyst, it was found that the longest catalyst life is attained under the lowest pressure for liquefying the olefins.$^{7)}$

In this paper, the disproportionation of propylene or 1-butene was carried out in order to compare the effect of the reaction pressure on the catalytic activity of MoO_3–Al_2O_3 with that of Re_2O_7–Al_2O_3 in the pressure range from 1.0 to 130 kg/cm^2.

Experimental

The MoO_3–Al_2O_3 catalyst was prepared in the way reported in the previous papers.$^{2-4)}$ The Re_2O_7–Al_2O_3 catalyst was obtained by impregnating the 20% Re content of $HReO_4$ with γ-Al_2O_3 and by then calcining it at 550 °C for 5 h. The atomic ratio of Re to Al was 1: 25, the same as that of Mo to Al in the case of the MoO_3–Al_2O_3 catalyst. The pretreatment of catalysts before starting the reaction was carried out in a flow of oxygen or air for a few hours, and then in a flow of nitrogen for several hours at 600 °C.

A conventional flow system with a fixed catalyst bed was used as the experimental apparatus. The upper and lower sections of the catalyst bed were filled with γ-Al_2O_3. The reaction products were analyzed by gas chromatography, as has been reported in the previous papers.$^{2-4)}$

Results and Discussion

Effects of Pressure. The disproportionation of propylene over the MoO_3–Al_2O_3 catalyst in the pressure range from 1.0 to 130 kg/cm^2 is shown as Figs. 1 and 1′. The relationship of the maximum conversion (Max_{conv}), the time when the conversion attains to its maximum value (T_{max}), and the time when the conversion falls to half its maximum value ($\tau_{1/2}$) is shown in Fig. 2. In both the gas-phase reactions at various GHSV values and the liquid-phase reaction as the same LHSV, the maximum conversion increased with the increase in the pressure, while T_{max} and $\tau_{1/2}$ decreased. In the reaction at 1.05 kg/cm^2, the catalytic activity was markedly more elongated than that at higher pressures. This phenomenon is in good agreement with the following equation suggested by Milanovic and his co-workers:$^{9)}$

$$r = \text{Conversion} \times D/22400 \times 273/T \times P/760 \times 1/m$$

D: Total flow rate (ml/h)
T: Reactant temperature (K)
P: Reactant pressure (Torr)
m: Catalyst weight (g).

The molar ratio of butenes to ethylene was 1.03 at 1.05

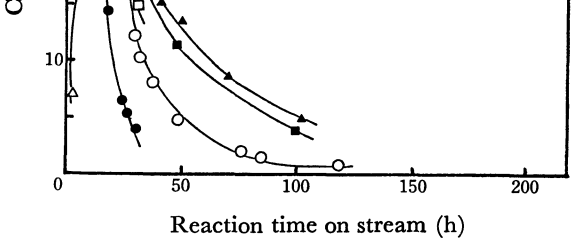

Fig. 1. Effect of pressure on the activity of MoO_3–Al_2O_3 catalyst in the disproportionation of propylene at 80 °C.
●: 130 kg/cm^2, LHSV=30, ○: 80 kg/cm^2, LHSV =30, ■: 50 kg/cm^2, LHSV=30, □: 30 kg/cm^2, GHSV =360, ▲: 15 kg/cm^2, GHSV=720, △: 1.05 kg/cm^2, GHSV=2520.

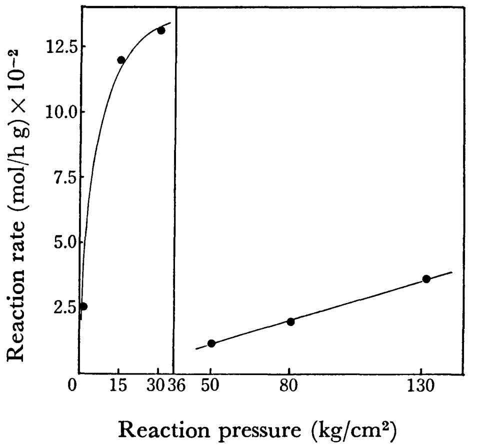

Fig. 1′. Effect of pressure on the activity of MoO_3–Al_2O_3 catalyst in the disproportionation of propylene at 80 °C (calculated from Milanovic's equation).

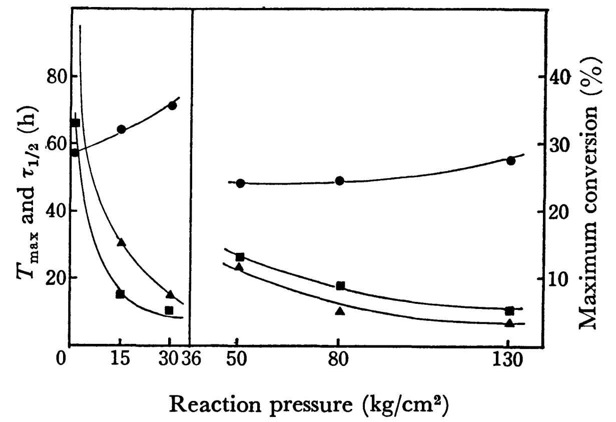

Fig. 2. Effect of pressure on the disproportionation of propylene at 80 °C.
▲: Reaction time when the conversion falls to half its maximum value ($\tau_{1/2}$), ■: reaction time when the conversion attains to maximum value (T_{max}), ●: maximum conversion.

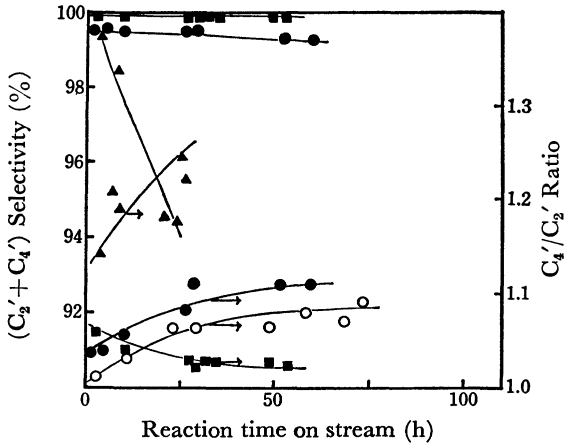

Fig. 3. Effect of pressure on the various values in the disproportionation of propylene over MoO_3–Al_2O_3 catalyst at 80 °C.
▲: 130 kg/cm², ●: 30 kg/cm², ○: 15 kg/cm², ■: 1.05 kg/cm².

kg/cm², but 1.24 at 130 kg/cm². On the other hand, the selectivity to ethylene and butenes under 130 kg/cm² was 94.5%, showing that the selectivity to ethylene and butenes decreases with an increase in the reaction pressure, as is shown in Fig. 3. The amount of the polymers formed over the MoO_3–Al_2O_3 catalyst increased with the reaction pressure. This suggests that the degradation of the catalytic activity results from the polymers formed over the catalyst.[3,4]

We reported in the previous papers[3,4] that the catalyst life of MoO_3–Al_2O_3 was elongated in the presence of solvents and that heptane was the most effective. This indicates that the surface of the MoO_3–Al_2O_3 catalyst is kept clean in the presence of solvents. In the presence of heptane, the effect of the pressure on the conversion of propylene is shown in Fig. 4. At every pressure, the catalyst life of MoO_3–Al_2O_3 was remarkably elongated by the addition of heptane.

The time when the conversion attains to its maximum values under 15 kg/cm² was about twice that under

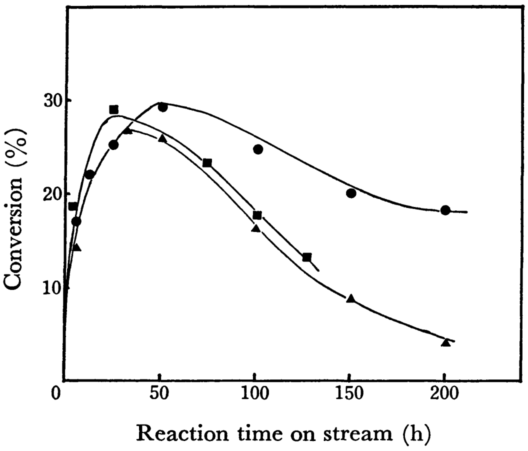

Fig. 4. Effect of pressure on the activity of MoO_3–Al_2O_3 catalyst in the disproportionation of propylene in the presence of heptane at 80 °C.
▲: 50 kg/cm², ■: 30 kg/cm², ●: 15 kg/cm².

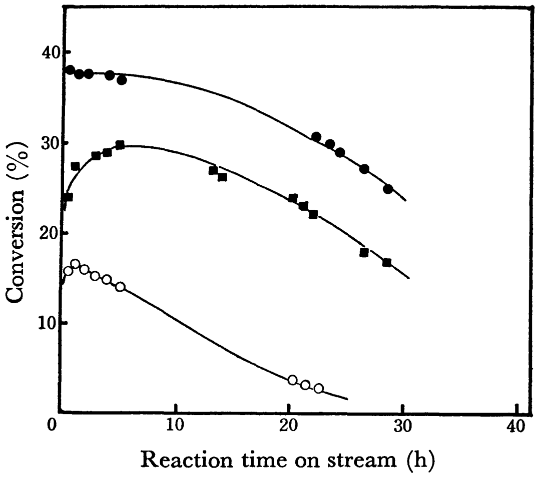

Fig. 5. Gas phase disproportionation of propylene at GHSV=350.
●: Re_2O_7–Al_2O_3, 40 °C, ■: Re_2O_7–Al_2O_3, 0 °C,
○: MoO_3–Al_2O_3, 40 °C.

50 kg/cm^2. However, it was not observed that the maximum conversion was greatly affected by the reaction pressure. The time when the conversion falls to half its maximum value under 15 kg/cm^2 was approximately 400 h, five times longer than that under 50 kg/cm^2.

Gas-phase Reaction of Propylene. In the disproportionation of propylene over the Re_2O_7–Al_2O_3 catalyst, the catalytic activity changed with the reaction time as is shown in Fig. 5. In the reaction at 80 °C the conversion showed approximately the equilibrium value of 44.0%. At the same GHSV of 350, the catalytic activity of the Re_2O_7–Al_2O_3 catalyst was twice the value of the MoO_3–Al_2O_3 catalyst and decreased rather slowly with the reaction time. Even at 0 °C, the Re_2O_7–Al_2O_3 was a considerably active catalyst.

The ratio of *trans*-2-butene to *cis*-2-butene showed a lower value than the equilibrium value at every temperature, indicating that the amount of *trans*-2-butene formed increases with the reaction temperature. The selectivity to ethylene and butenes was 99.5% at a steady state, and the molar ratio of butenes to ethylene was approximately 1.0. These facts show that the disproportionation over the Re_2O_7–Al_2O_3 catalyst is highly selective. The apparent activation energy of the Re_2O_7–Al_2O_3 catalyst obtained from the Arrhenius plots was 2.51 kcal/mol, lower than the 4.09 kcal/mol of the MoO_3–Al_2O_3 catalyst. The selectivity to ethylene and butenes or the ratio of butenes to ethylene was not much affected by the reaction temperature. The ratio of 1-butene in the butenes produced over Re_2O_7–Al_2O_3 was lower than that over MoO_3–Al_2O_3. This seems to show that the Re_2O_7–Al_2O_3 catalyst has fewer active sites for isomerization.

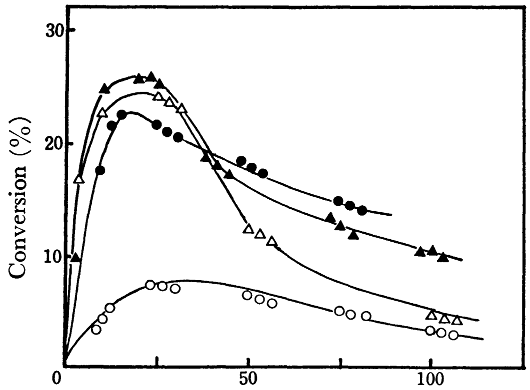

Fig. 6. Comparison of the activity of MoO_3–Al_2O_3 catalyst with that of Re_2O_7–Al_2O_3 catalyst.
△: MoO_3–Al_2O_3, 80 °C, ○: MoO_3–Al_2O_3, 40 °C, ▲: Re_2O_7–Al_2O_3, 80 °C, ●: Re_2O_7–Al_2O_3, 40 °C.

Liquid-phase Reaction of Propylene. In the reaction over Re_2O_7–Al_2O_3 and MoO_3–Al_2O_3 under 50 kg/cm^2, the catalytic activity changed as is shown in Fig. 6. The difference in catalytic activity between Re_2O_7–Al_2O_3 and MoO_3–Al_2O_3 at 80 °C seems not to be significant. However, in the reaction at 40 °C, the difference becomes larger, suggesting that the difference in apparent activation energy between Re_2O_7–Al_2O_3 and MoO_3–Al_2O_3 is larger than in the case of the gas-phase disproportionation. It can be assumed that Re_2O_7–Al_2O_3 offers a lower activation energy than MoO_3–Al_2O_3. The selectivity to ethylene and butenes in the disproportionation over Re_2O_7–Al_2O_3 at 40 °C was entirely 100%, with the ratio of butenes to ethylene nearly 1.0.

In the liquid-phase reaction, the selectivity to ethylene and butenes was lower than in the gas-phase reaction. This shows that polymerization of propylene or ethylene increases with the reaction pressure, the ratio of butenes to ethylene having a larger value than that in the gas phase. The ratio of *trans*-2-butene to *cis*-2-butene showed a little higher value. It seems that, in the liquid-phase disproportionation, the desorption from the surface of the catalyst does not proceed easily and that the steric hindrance in the reaction is larger than in the gas phase.[10)]

As has been mentioned above, it was concluded that the pressure increase in the liquid-phase disproportionation enhances the reaction rate.*

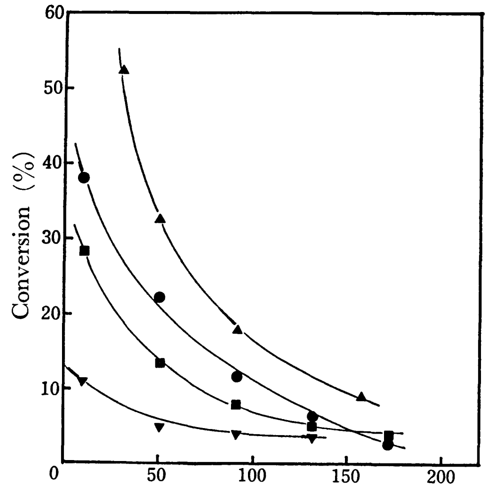

Fig. 7. Dispropornation of 1-butene in the gas phase over Re_2O_7–Al_2O_3 catalyst at GHSV=2000.
▲: 140 °C, ●: 80 °C, ■: 40 °C, ▼: 0 °C.

Gas-phase Reaction of 1-Butene. In the range from 0 to 140 °C, the catalytic activity of Re_2O_7–Al_2O_3 was the highest at 140 °C (Fig. 7); it decreased markedly with a decrease in the reaction temperature. At any temperature the catalytic activity of Re_2O_7–Al_2O_3 was higher than that of MoO_3–Al_2O_3. In the disproportionation of 1-butene, the reaction scheme can be written as follows:

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* The relationship between the equilibrium constant K and the pressure P (molar concentration) can be written as follows:[8)]

$$\frac{\partial RT\ln K}{\partial P} = -\Delta V.$$

ΔV will have a large negative value in a polymerization where the difference in molecular volume between the original system and the production system is quite high.

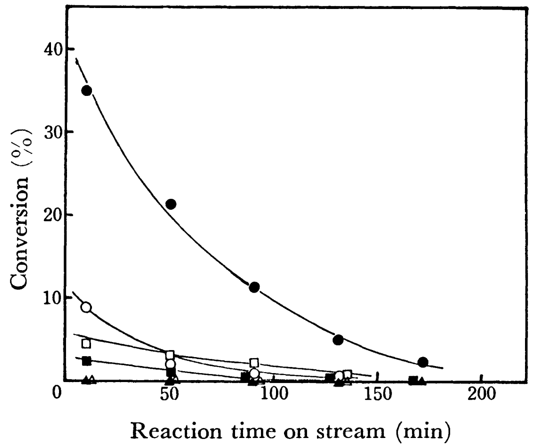

Fig. 8. Disproportionation of 1-butene in the gas phase at 80 °C and GHSV=2000.
Re_2O_7–Al_2O_3: ● Disproportionation, ■ isomerization, ▲ hydrogenation,
MoO_3–Al_2O_3 : ○ disproportionation, □ isomerization, △ hydrogenation.

$$2\ 1\text{-}C_4H_8 \xrightarrow{D_1} C_2H_4 + 3\text{-}C_6H_{12} \qquad (D_1)$$

$$1\text{-}C_4H_8 \xrightarrow{I} 2\text{-}C_4H_8 \qquad (I)$$

$$C_2H_4 + 2\text{-}C_4H_8 \xrightarrow{D_2} 2\ C_3H_6 \qquad (D_2)$$

$$1\text{-}C_4H_8 + 2\text{-}C_4H_8 \xrightarrow{D_3} C_3H_6 + 2\text{-}C_5H_{10} \qquad (D_3)$$

$$2\text{-}C_6H_{12} + 1\text{-}C_4H_8 \xrightarrow{D_4} C_3H_6 + C_7H_{14} \qquad (D_4)$$

$$2\ C_3H_6 \xrightarrow{P_1} C_6H_{12} \qquad (P_1)$$

$$C_2H_4 + C_3H_6 \xrightarrow{P_2} C_5H_{10} \qquad (P_2)$$

$$1\text{-}C_4H_8 \xrightarrow{Deh} [C_4H_{8-x}] + x/2\ H_2 \qquad (Deh)$$

$$1\text{-}C_4H_8 + H_2 \xrightarrow{Hyd} n\text{-}C_4H_{10} \qquad (Hyd)$$

The disproportionation of 1-butene over MoO_3–Al_2O_3 and Re_2O_7–Al_2O_3 is shown in Fig. 8. The relative reactivities in the various reactions may be shown as follows:

Disproportionation ($C_2'+C_6'$)	MoO_3–Al_2O_3 $<$ Re_2O_7–Al_2O_3
Isomerization (2-C_4')	$\gg$
Hydrogenation (C_4H_{10})	≈ 0

At a conversion of 13.0%, Re_2O_7–Al_2O_3 showed a higher selectivity to ethylene and hexenes than MoO_3–Al_2O_3, as is shown in Fig. 9. Moreover, the relationship between the yield of the disproportionation products and the yield of the isomerization products is shown in Fig. 10. These figures indicate that a more selective disproportionation occures over the Re_2O_7–Al_2O_3 catalyst than over MoO_3–Al_2O_3.

Liquid-phase Reaction of 1-Butene. The liquid-phase disproportionation of 1-butene over MoO_3–Al_2O_3 was very different from the reaction of propylene. That is to say, in the former case saturated hydrocarbons, such as butane, propane, and isobutane, were produced.[4] The hydrogen produced by dehydrogenation (Deh.) will result in the formation of saturated

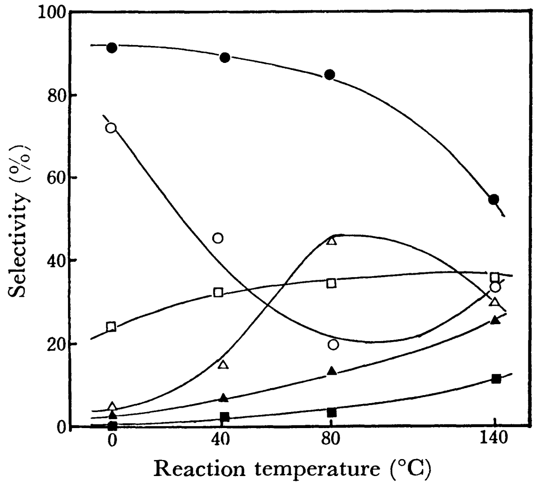

Fig. 9. Disproportionation of 1-butene in the gas phase at 13.0% of conversion.
Re_2O_7–Al_2O_3: ● $C_2'+C_6'$, ▲ $C_3'+C_5'$, ■ 2-C_4'
MoO_3–Al_2O_3: ○ $C_2'+C_6'$, △ $C_3'+C_5'$, □ 2-C_4'.

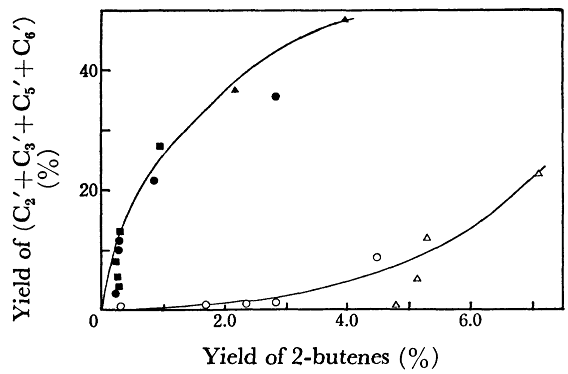

Fig. 10. Disproportionation of 1-butene in the gas phase over Re_2O_7–Al_2O_3 and MoO_3–Al_2O_3 catalyst.
Re_2O_7–Al_2O_3: ▲ 140 °C, ● 80 °C, ■ 40 °C,
MoO_3–Al_2O_3: △ 140 °C, ○ 80 °C.

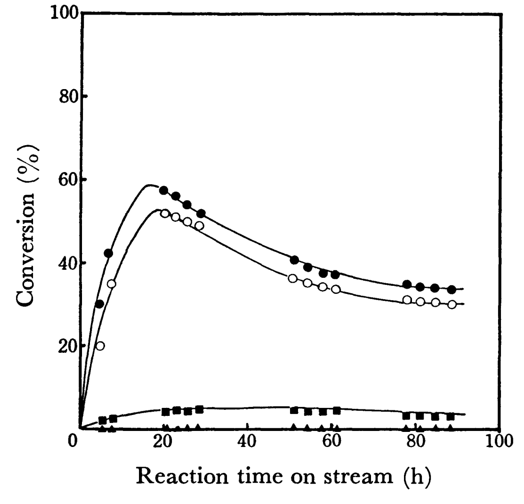

Fig. 11. Liquid phase disproportionation of 1-butene under 50 kg/cm² at 80 °C and LHSV=40.
Re_2O_7–Al_2O_3: ●Total conversion, ○disproportionation, ■isomerization, ▲hydrogenation.

hydrocarbons.[11] From the product distribution, it is estimated that the reaction of 1-butene proceeds not only by means of the D_1 reaction but also by means of the D_3 reaction.

On the other hand, the total conversion over Re_2O_7–Al_2O_3 has shown a maximum at 20 h, then it gradually decreased. Most of the reaction products over Re_2O_7–Al_2O_3 derived from the disproportionation. The difference between the two catalysts for isomerization (I) was not observed clearly, but the catalytic activity of Re_2O_7–Al_2O_3 for hydrogenation was markedly smaller.

From these facts, it seems that the Re_2O_7–Al_2O_3 catalyst is preferable to MoO_3–Al_2O_3 for the disproportionation of 1-butene.

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