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Disproportionation of Propylene over MoO_3-SiO_2 Catalyst with Various Treatments

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Disproportionation of propylene over MoO_3–SiO_2 (atomic ratio: Mo/Si=1/25) catalyst treated with HCl and aqueous ammonia was studied in the temperature range 350—600 °C under atmospheric pressure. The activity of MoO_3–SiO_2 catalyst extracted with aqueous ammonia remained for a long time, since most of free MoO_3 was removed from the MoO_3–SiO_2 surface. This gave rise to increase in the selectivity for disproportionation of propylene to ethylene and butenes and decrease in the selectivity for hydrogenation, isomerization and polymerization. When MoO_3–SiO_2 not subjected to treatment was pretreated by H_2 gas, it showed higher catalytic activity and lower selectivity for disproportionation than the one treated by N_2 gas.

In previous papers[1–4] we reported that MoO_3–Al_2O_3 shows high catalytic activity for the olefin disproportionation in the temperature range 100—200 °C and that Re_2O_7–Al_2O_3 has high catalytic activity even at ambient temperature. Ogasawara *et al.* reported that the pretreatment by H_2 gas makes active MoO_3–SiO_2 catalyst which has much free MoO_3 on its surface.[5] It is assumed that the free MoO_3 accompanies side reactions such as polymerization and hydrogenation which cause the catalytic degradation.[6] We have carried out disproportionation of propylene using MoO_3–SiO_2 catalyst treated with HCl and aqueous ammonia at relatively high temperatures.

The oxidation states of transition metal affect the catalytic activity of the disproportionation of olefins. It is known that MoO_3–Al_2O_3 catalyst is highly active even in hexa-valent state, and the lower the oxidation state of Mo, the greater the decrease in catalytic activity. It has been reported that the oxidation value of Mo over MoO_3–SiO_2 catalyst is lower than that over MoO_3–Al_2O_3.[7] We wish to consider the difference in oxidation state of Mo between the case of pretreatment of MoO_3–SiO_2 by H_2 and that by N_2.

Experimental

The MoO_3–SiO_2 catalyst was prepared by impregnating a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution with silica which was evaporated to dryness "Snowtex" (Nissan Kagaku Co., Ltd.), and then by calcining in a flow of air at 550 °C for 5 h. The atomic ratio of Mo to Si was 1: 25, the same as that of Mo to Al, and Re to Al previously reported (A and B catalyst without treatment).[1–4]

The MoO_3–SiO_2 catalysts (C′, C″, C‴) were extracted with aqueous ammonia of various concentrations for 24 h. They were first filtered and washed with water, and then evaporated to dryness prior to calcination in a flow of air at 550 °C for 5 h. The catalysts (D′, D″) treated with HCl solution were evaporated to dryness in a flow of N_2 gas at 100 °C and then calcined at 550 °C for 1 h in a stream of air.

After pretreatment of the A catalyst with N_2 gas and the other catalysts with H_2 gas for 2 h, the reaction was carried out by the conventional fixed bed flow system with a U type reactor in the temperature range 350—600 °C. The reaction products were periodically analyzed by a gas chromatogram connected to the reaction system.

Results and Discussion

Effects of Various Treatments of MoO_3–SiO_2 on the Catalytic Activity. The profiles of the activity change of propylene disproportionation over MoO_3–SiO_2 catalyst with various treatments are shown in Fig. 1. In the initial reaction time, the catalytic activity for the disproportionation was in the order MoO_3–SiO_2 treated with HCl>MoO_3–SiO_2 without treatment>MoO_3–SiO_2 extracted with aqueous ammonia. The activity of catalysts extracted with aqueous ammonia differs greatly from that of catalysts not subjected to such treatment but treated with HCl solution. In the former case, the catalytic activity shows a maximum value at 25 min of the reaction time and then decreases gradually. Even after 20 h, its activity remains high. In the latter case

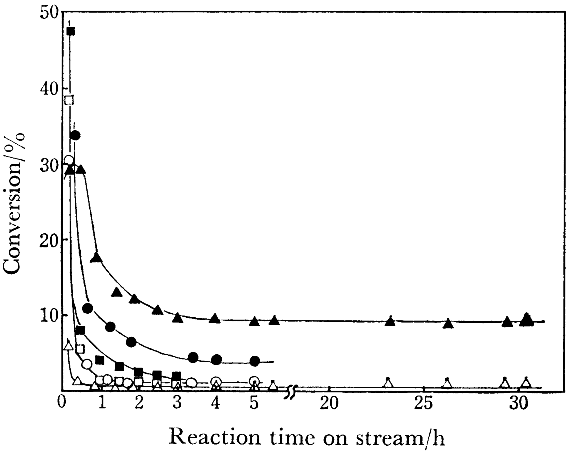

Fig. 1. Effect of various treatments of MoO_3–SiO_2 catalyst on the gas phase disproportionation of propylene at 500 °C and GHSV=60 (h^{-1}).
MoO_3–SiO_2 catalyst without treatment;
●: disproportionation, ○: hydrogenation.
MoO_3–SiO_2 catalyst extracted with 5 % aqueous ammonia;
▲: disproportionation, △: hydrogenation.
MoO_3–SiO_2 catalyst treated with 5 % HCl solution;
■: disproportionation, □: hydrogenation.

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the catalytic activity decreases rapidly with the reaction time. The catalytic activity for hydrogenation over MoO_3–SiO_2 extracted with aqueous ammonia was suppressed and the disproportionation to ethylene and butenes was promoted.

Effects of Reaction Temperature. In the temperature range 350—6000 °C, the activity for the disproportionation and hydrogenation of propylene changes within 60 min (Figs. 2—4). At all temperatures examined, the activity of the catalyst extracted with aqueous ammonia for the disproportionation shows a maximum value at 25 min. The new active sites seem to be formed by the reduction of the catalyst with H_2 or aqueous ammonia. At 600 °C, the catalytic activity remains unchanged during the course of reaction. At temperatures below 400 °C, the activity for the disproportionation becomes much lower. This indicates that the suitable reaction temperatures for the disproportionation are above 450 °C.

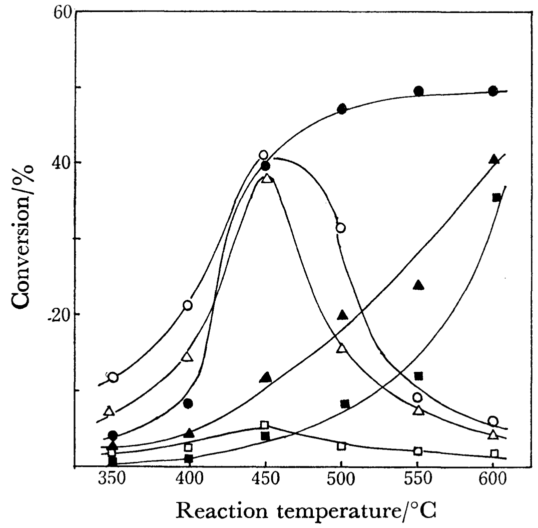


Fig. 2. Effect of temperature on the catalytic activity of MoO_3–SiO_2 without treatment in the gas phase disproportionation at GHSV=60 (h^{-1}).
Disproportionation; ●: 10 min, ▲: 25 min, ■: 60 min.
Hydrogenation; ○: 10 min, △: 25 min, □: 60 min.

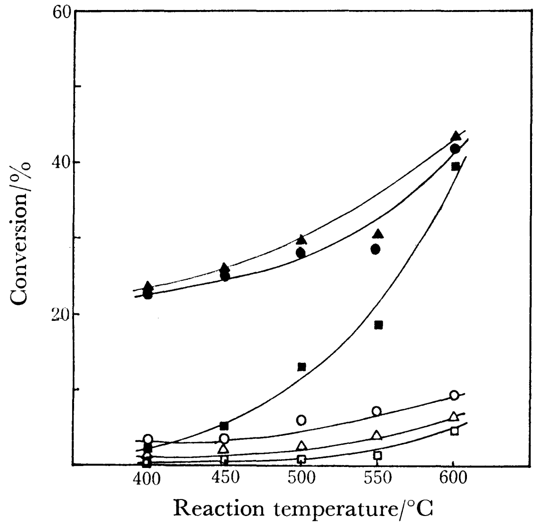


Fig. 3. Effect of temperature on the catalytic activity of MoO_3–SiO_2 extracted with 5 % aqueous ammonia in the gas phase disproportionation at GHSV=60 (h^{-1}).
Disproportionation; ●: 10 min, ▲: 25 min, ■: 60 min.
Hydrogenation; ○: 10 min, △: 25 min, □: 60 min.

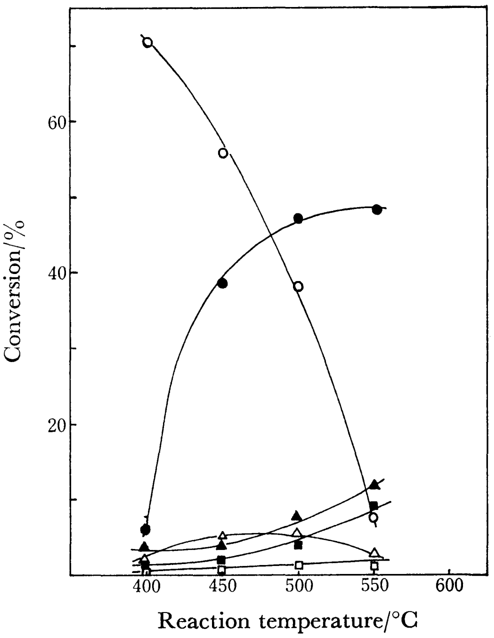


Fig. 4. Effect of temperature on the catalytic activity of MoO_3–SiO_2 treated with 5 % HCl solution in the gas phase disproportionation at GHSV=60 (h^{-1}).
Disproportionation; ●: 10 min, ▲: 25 min, ■: 60 min.
Hydrogenation; ○: 10 min, △: 25 min, □: 60 min.

The mode of activity change for hydrogenation reaction vary with catalyst. In the catalyst not subjected to treatment, the activity for the hydrogenation becomes maximum at 450 °C.

Effects of Concentration of Aqueous Ammonia. The initial activity of the catalyst extracted with various concentrations of aqueous ammonia is shown in Fig. 5.

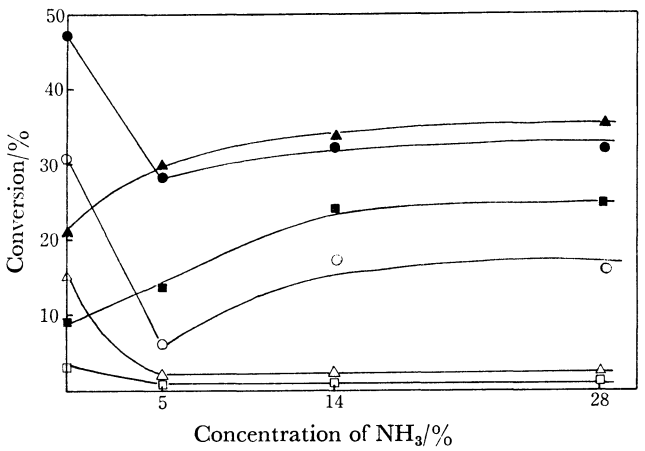


Fig. 5. Effect of concentration of aqueous ammonia on the catalytic activity of MoO_3–SiO_2 in the disproportionation of propylene at 500 °C and GHSV=60 (h^{-1}).
Disproportionation; ●: 10 min, ▲: 25 min, ■: 60 min.
Hydrogenation; ○: 10 min, △: 25 min, □: 60 min.

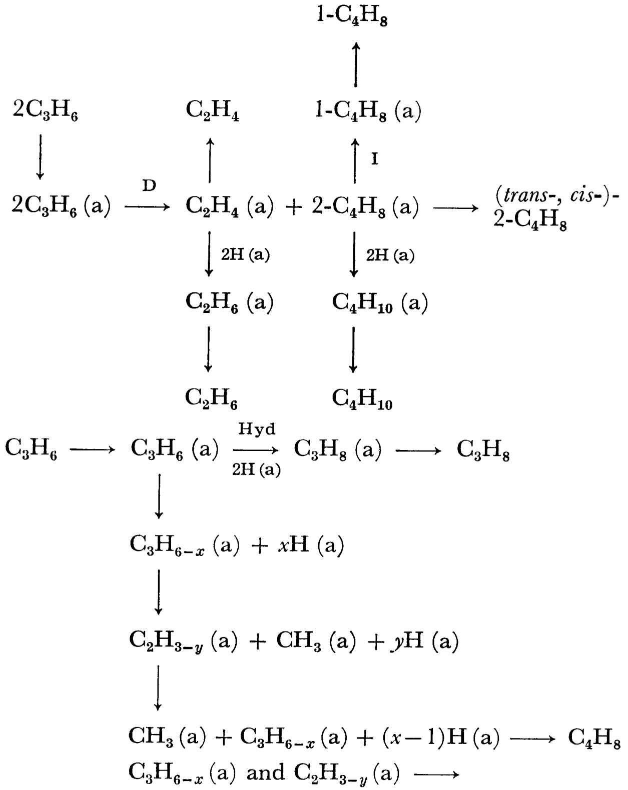
In each case, the catalytic activity after 10 min was lower than that not subjected to treatment. This seems to be due to the decrease of Mo metal by the extraction with aqueous ammonia. After 25 min the activity of the catalyst extracted with aqueous ammonia had higher value than that of the other catalysts. It seems that the hydrogenation over MoO_3–SiO_2 extracted with aqueous ammonia is suppressed, and the active sites for the disproportionation increase.

The hydrogenation decreased gradually with increase in reaction time. Yermakov *et al.* suggested that the oxidation state of Mo for the disproportionation or polymerization is +4, and that for hydrogenation is +2.[8] It seems that many active sites are formed for the disproportionation, the oxidation state of Mo being +4, but few for hydrogenation, the oxidation state of Mo being +2.

After removal of the free MoO_3 over MoO_3–SiO_2 catalyst by leaching with aqueous ammonia, the activity for the disproportionation remained unchanged as shown in Fig. 5. It is assumed that the increase in the acidity of the catalyst is due not to SiO_2 or MoO_3, but to the new acidic sites formed by the interaction of the two. The free MoO_3 can be extracted with aqueous ammonia. In the case of MoO_3–Al_2O_3 catalyst, 80% of free MoO_3 is removed from the catalyst surface, whereas in the MoO_3–SiO_2, 30% of free MoO_3 is taken off from the surface of MoO_3–SiO_2.[5] Vaghi *et al.* reported that the removal of polymolybdate by leaching with aqueous ammonia restores the activity in the tetrahedral Mo(VI) region, and the decomposition of the molybdosilicate anion occurs at pH 10.[9,10] From our results, it seems that leaching of MoO_3–SiO_2 with aqueous ammonia prefers the removal of free MoO_3 to the decomposition of Mo–O–Si bonds.

Product Distribution. An example of products distribution is given in Table 1. The catalysts extracted with aqueous ammonia (C′, C″, C‴) exhibit higher selectivity to ethylene and butenes as compared with the catalysts, the one without treatment and the other with treatment by HCl (D′, D″). On the other hand, the selectivity for hydrogenation of propylene to propane over MoO_3–SiO_2 extracted with aqueous ammonia is lower than that of the other catalysts. The isomerization of 2-butene to 1-butene produced *via* the disproportionation over the catalysts treated with aqueous ammonia decreases. This shows that the disproportionation over the catalysts subjected to aqueous ammonia extraction is promoted more selectively by suppression of self-hydrogenation or polymerization.[11,12]

The difference in products distribution between the catalyst pretreated by H_2 (A) and that by N_2 (B) shows that the oxidation state of Mo for each case is different. It may be assumed that the oxidation state of Mo in the case of H_2 becomes +4 according to Yermakov *et al.*[8]



D: Disproportionation, I: isomerization, Hyd: hydrogenation, (a): adsorbed species.

Reaction Scheme.

Table 1. Products distribution in the gas phase disproportionation of propylene over MoO_3–SiO_2 catalyst at 500 °C and GHSV=60 (after 25 min of reaction)

Catalyst	A[a]	B[b]	C′[c]	C″[c]	C‴[c]	D′[d]	D″[d]
Conversion for disproportionation (%)	17.3	6.23	29.0	32.8	35.7	7.63	6.51
(C_2+C_2'+C_4+C_4') selectivity (%)	60.5	80.7	92.2	92.4	90.0	58.5	62.2
(C_4+C_4')/(C_2+C_2') ratio	0.183	0.231	0.757	0.603	0.641	0.172	0.153
C_4'/C_2' ratio	0.380	0.675	0.807	0.660	0.711	0.391	0.373
C_2/(C_2+C_2') (%)	53.0	68.0	7.62	9.93	11.8	60.5	63.3
C_4/(C_4+C_4') (%)	15.5	6.74	1.59	1.42	2.10	10.2	10.6
1-C_4'/C_4' (%)	46.8	47.2	31.0	39.9	42.5	39.6	47.2
trans-/*cis*- ratio in 2-C_4'	1.33	1.31	1.30	1.34	1.35	1.30	1.31
Conversion for hydrogenation (%)	15.2	1.42	0.90	1.55	2.38	5.29	3.80
C_3 selectivity (%)	40.7	18.5	3.31	4.53	6.26	40.9	36.9

a) Pretreated with H_2. b) Pretreated with N_2. c) Extracted with 5% aqueous ammonia (C′), 14% aqueous ammonia (C″), and 28% aqueous ammonia (C‴). d) Treated with 5% HCl (D′) and 14% HCl solution (D″).

Since the ratio of (C_4+C_4') to (C_2+C_2') is lower than C_4'/C_2' and the ratio of C_2 to (C_2+C_2') is larger than that of C_4 to (C_4+C_4'), hydrogenation of ethylene to ethane proceeds more rapidly than that of butenes to butane during the course of disproportionation. The ratio of *trans*- to *cis*- in 2-butenes approximates to equilibrium value at each reaction temperature.

In the catalyst subjected to aqueous ammonia extraction, the molar ratios C_4'/C_2' and $(C_4+C_4')/(C_2+C_2')$ in the temperature range 400—600 °C decrease with increase in the reaction temperature (Fig. 6). At all temperatures, the values increase with reaction time. In the initial reaction periods, the desorption of C_4 and C_4' from the catalyst surface is more difficult than that of C_2 and C_2', the decomposition of C_4 and C_4' proceeding very rapidly at high temperature.

The molar ratios C_4'/C_2' and $(C_4+C_4')/(C_2+C_2')$ for the catalysts treated with aqueous ammonia are greater than those not subjected to such treatment but treated with HCl. It seems that the active sites for disproportionation are formed. In the reaction below 450 °C, the ratio C_4'/C_2' or $(C_4+C_4')/(C_2+C_2')$ after 25 min of the reaction is approximately 1.0, indicating the most selective disproportionation.

The molar ratios of 1-butene in all butenes are shown in Fig. 7. At temperatures below 550 °C, each ratio in the catalyst extracted with aqueous ammonia is the lowest among the catalysts subjected to various treatments. The ratio in the case of the catalyst treated with HCl is lower than that of the catalyst not subjected to treatment. Decrease in the ratio in aqueous ammonia shows that acid sites are necessary for the isomerization over MoO_3–SiO_2 catalyst. On the other hand, HCl which neutralizes basic sites is also effective for decreasing the isomerization activity of MoO_3–SiO_2 catalyst. This suggests that both acid and basic sites function effectively in isomerization of 2-butenes to 1-butene over MoO_3–SiO_2 catalyst.

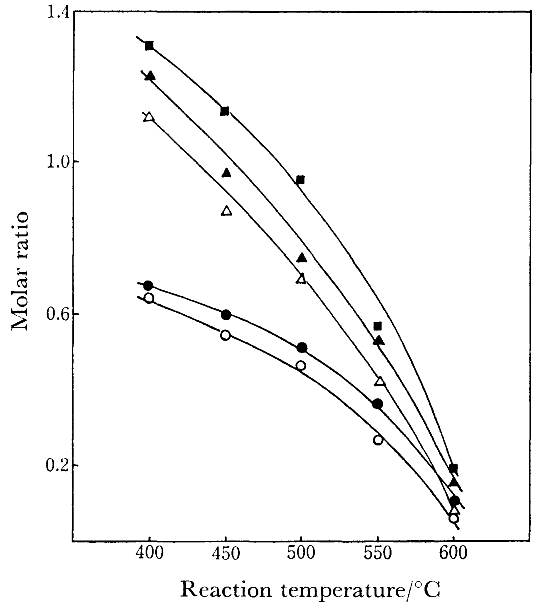


Fig. 6. Effect of temperature on C_4'/C_2' and $(C_4+C_4')/(C_2+C_2')$ molar ratio in the disproportionation of propylene over MoO_3–SiO_2 catalyst extracted with 5 % aqueous ammonia.

Reaction after 10 min; ●: C_4'/C_2', ○: $(C_4+C_4')/(C_2+C_2')$, 25 min; ▲: C_4'/C_2', △: $(C_4+C_4')/(C_2+C_2')$, 300 min; ■: C_4'/C_2'.

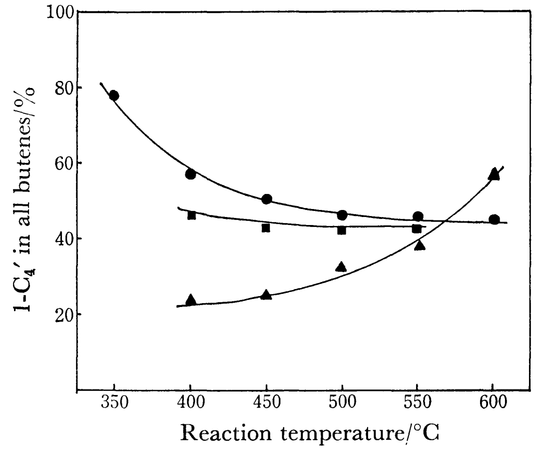


Fig. 7. Effect of temperature on molar ratio of 1-butene in all butenes in the gas phase disproportionation over MoO_3–SiO_2 catalyst at GHSV=60 (h^{-1}) after 25 minutes of reaction time.

●: MoO_3–SiO_2 catalyst. ▲: MoO_3–SiO_2 catalyst extracted with 5 % aqueous ammonia. ■: MoO_3–SiO_2 catalyst treated with 5 % HCl solution.

The behavior of MoO_3–SiO_2 catalyst in the shift of the double bond from 2-butenes to 1-butene may be explained as follows.[13] The mechanism of this reaction involves the existence of an electron accepting (oxidative, *i.e.*, acid) center in the vicinity of the π-bond between carbons 2 and 3 and the presence of an electron donating (reducing, *i.e.*, basic) center in the vicinity of the σ-bond between carbons 1 and 2. The shift of the double bond is of a concerted type.

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