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Preparation of Highly Active Sulfided Mo/Al_2O_3 Catalyst for Hydrogenation of Cyclopropane and Olefins

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The effect of sulfiding with H_2S on the activity of Mo/Al_2O_3 catalyst in the hydrogenation of cyclopropane and various olefins was investigated. Extremely high active sulfided Mo/Al_2O_3 catalyst was prepared by sulfiding of Mo/Al_2O_3 with H_2S followed by evacuation under high vacuum at 450 °C.

Molybdenum based catalyst such as $Co/Mo/Al_2O_3$ and $Ni/Mo/Al_2O_3$ are commonly used in heavy oil upgrading after sulfiding with H_2S.1) Generally, these presulfided catalysts show high and stable activity for petroleum refining processes.1) Sulfiding treatment is one useful method to improve the catalytic activity for Mo based catalysts. In the present paper, we report the effect of presulfiding with H_2S and post-treatment by evacuation on the activity of Mo/Al_2O_3 catalyst in the hydrogenation of cyclopropane and various olefins.

A conventional closed circulation system (385 ml) was used. 0.3 g of Mo/Al_2O_3 catalyst prepared by impregnation (12.5 wt% MoO_3) was evacuated at 500 °C for 2 h in the reaction vessel. The catalyst was reduced with hydrogen (50 Torr) at 450 °C for 2 h and then sulfided with H_2(50 Torr)-H_2S(20 Torr) mixture at 450 °C for 2 h, followed by evacuation at different vacuum levels (10^{-3} or 10^{-5} Torr) as post-treatment. Reaction products were analyzed by a gaschromatograph equipped with propylene carbonate column (5 m) at 0 °C.

Table 1 shows the effect of post-treatment on the activity of reduced and sulfided Mo/Al_2O_3 catalysts in the hydrogenation of cyclopropane. The catalytic activity of reduced Mo/Al_2O_3 followed by evacuation at 10^{-5} Torr was significantly higher than that evacuated at 10^{-3} Torr. Although the metathesis of propylene formed by the isomerization of cyclopropane proceeded simultaneously, no remarkable difference in the product distribution on the two reduced catalysts was observed. The activity of reduced Mo/Al_2O_3 catalyst was markedly suppressed by sulfiding with H_2S, followed by evacuation at 10^{-3} Torr, and no metathesis reaction occurred. However, sulfided Mo/Al_2O_3 catalyst and evacuation at 10^{-5} Torr showed higher activity for the hydrogenation of cyclopropane at 0 °C than Pt/Al_2O_3 catalyst and only propane was formed. Highly active Mo/Al_2O_3 catalyst could be prepared by sulfiding of Mo/Al_2O_3 with H_2S followed by evacuation under high vacuum at 450 °C. We refer to this highly active catalyst as " highly active sulfided Mo/Al_2O_3 catalyst.

Table 1. Effect of pretreatment and post-treatment of Mo/Al_2O_3 catalyst on hydrogenation of cyclopropane(CP)a)

Catalyst	Pretreatment	Post-treatment (Evacuation)	Reaction temp/°C	Activity % $g^{-1}min^{-1}$	Selectivity/% C_3H_6	C_3H_8	C_2H_4 + C_4H_8	C_4H_{10}
Mo/Al_2O_3	Reduction	10^{-3} Torr c)	100	1.09	7	76	12	5
	Reduction	10^{-5} Torr d)	100	9.56	8	64	20	8
	Sulfiding	10^{-3} Torr c)	100	0.28	32	68	0	0
	Sulfiding	10^{-5} Torr d)	0	11.11	0	100	0	0
Pt/Al_2O_3 b)	Reduction	10^{-4} Torr e)	0	0.53	0	100	0	0

a) CP : H_2 = 10 Torr : 10 Torr. b) Japan Engelhard Co., DASH-220. c) 450 °C for 0.5 h. d) 450 °C for 2 h. e) 450 °C for 1 h.

Table 2 shows the activity of highly active sulfided Mo/Al_2O_3 catalyst for the hydrogenation of various olefins. As can be seen in Table 2, highly active sulfided Mo/Al_2O_3 catalyst also showed high activity for the hydrogenation of various olefins even at low temperatures, as does cyclopropane.

Recently, Massoth et al.2) reported that molybdenum oxide with a monolayer formed on alumina surface in MoO_3/Al_2O_3 catalyst is converted to highly dispersed molybdenum disulfide with destruction of monolayer structure by sulfiding with H_2S. Tanaka et al.3) demonstrated that the coordinatively unsaturated sites of MoS_2 surface act as the active sites for the hydrogenation of unsaturated hydrocarbons. We found that Mo/S ratio in XPS spectra of sulfided Mo/Al_2O_3 catalyst after evacuation at 450 °C under 10^{-5} Torr (Mo/S = 3.01) indicated more removal of sulfur from catalyst surface than occurred at 10^{-3} Torr evacuation (Mo/S = 2.34). Thus, it is concluded that the extremely high activity of highly active sulfided Mo/Al_2O_3 catalyst for the hydrogenation of cyclopropane and olefins can be attributed to the formation of highly dispersed MoS_2 with low coordination number on sulfided Mo/Al_2O_3.

Table 2. Hydrogenation of various olefins over highly active sulfided Mo/Al_2O_3 catalyst

Olefin	Reaction temp/°C	Reaction time/min	Conversion %
Ethylenea)	0	5	100
	-47	15	100
	-75	15	100
Propylenea)	5	15	100
	-46	30	100
1-Butenea)	0	15	100
1,3-Butadieneb)	4	20	100
	-20	35	100

a) H_2 : olefin = 10 Torr : 10 Torr

b) H_2 : olefin = 20 Torr : 10 Torr; only butane was formed.

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