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Catalytic Functionalities of Molybdenum Catalysts Supported on Brazilian Bentonites

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Synopsis. Two kinds of Brazilian bentonites were applied to supports of molybdenum catalysts to improve the catalytic selectivities of the hydrotreating catalysts. Separate model tests reactions showed that bentonite-supported molybdenum catalysts have higher activities for hydrocracking and hydrodesulfurization as compared to a standard Al_2O_3 supported catalyst, while the Al_2O_3 was superior to the bentonites for hydrogenation activity.

Some kinds of natural clays such as bentonite, have been recognized as suitable for cracking catalysts. In fact, acid-treated clays of montmorillonite type were the first fluid cracking catalysts widely employed by the industry, though the clays were abandoned in favor of synthetic alumina and silica–alumina. Then zeolites came to dominate the petroleum refining industry. Recently, an application of molybdenum catalysts to hydrotreating of petroleum residue or coal derived oil has rekindled interest in these clays as the catalyst supports because of their large pores.

Sakata and Hamrim[1)] reported hydrodesulfurization(HDS) and hydrodenitrogenation(HDN) over several clays found in coal mineral matter. Takeuchi *et al.*[2)] showed that sepiolite-supported molybdenum catalysts are applicable to the hydrotreating of petroleum residue. Mochida *et al.*[3)] also mentioned roles of sepiolite as the support of nickel–molybdenum catalysts in the selective hydrotreating of solvent refined coal. With other clays as the support for molybdenum catalyst, catalytic functionalities of hydrotreating catalysts such as hydrocracking or hydrogenation, still remain unresolved, although a lot of patents were applied in this field. In the present paper, Brazilian bentonites were used as supports of molybdenum catalysts to improve the catalytic selectivity of hydrotreating catalyst. Hydrocracking of diphenylmethane(DPM), HDS of dibenzothiophene(DBT) and hydrogenation of 1-methylnaphtalene(1-MN) were performed under a high pressure of H_2 using bentonite-supported catalysts and a standard alumina-supported catalyst to elucidate their catalytic functionalities.

Experimental

Catalyst supports used in this experiment were two kinds of Brazilian bentonites (Bentonite S and V, Somipal S/A. Co.). These natural minerals were activated chemically with H_2SO_4 (35%), followed by washing until no sulfur could be detected. Then, the samples were heated at 500 °C for 3 h in a presence of air. A commercial type of γ-Al_2O_3 (Sumitomo Aluminium Co.), which was selected as a standard support in our work, was also used. Properties of the bentonites and the alumina are given in Table 1. A 10 wt% of MoO_3 catalysts were prepared by impregnating the carriers with a solution of ammonium heptamolybdate. After drying at 100 °C for 8 h, the samples were calcined at 500 °C for 1 h. Then the catalysts were presulfided in a stream of 10 vol% of H_2S (balance H_2) at 430 °C for 1 h before reaction.

For hydrocracking, HDS and hydrogenation, the reactions were carried out in a stainless steel microreactor (50 cm^3) charged with 10 cm^3 of the commercial reagent and 0.5 g of the catalyst. The unit was pressurized with H_2 to an initial pressure of 70 kg/cm^2 and then injected into an oven heated at 430 °C. Hydrocracking and HDS reactions were performed at 400 °C for 60 min, while 90 min of reaction were selected for hydrogenation. At least the reactions were done twice, and values given in Table 2 are averaged. Reaction products were analyzed by a gas cromatography (Shimadzu GC-6AM). More thorough analyses were done by obtaining mass spectra (Shimadzu GC–MS QP-1000) of the individual products.

Results and Discussion

The catalytic functionalities obtained on the various supports are summarized in Table 2.

Hydrocracking, HDS and hydrogenation activities for the sulfided molybdenum catalysts are given in Runs 1—4. MoS_2 catalyst supported on bentonite gave higher hydrocracking activities as compared to that on γ-Al_2O_3. Among the bentonite supports examined, hydrocracking activities of the catalysts increased after acid treatment of the bentonites. Bentonite S was superior to Bentonite V for hydrocracking of DPM.

Table 1. Properties of the supports

Sopport	Chemical composition/wt%								S.A.[a)]	P.V.[b)]
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	MgO	CaO	m^2 g^{-1}	ml g^{-1}
Bentonite S[c)]	69.6	14.4	8.0	1.38	2.16	3.39	0.15	0.52	95	0.15
Bentonite AS[d)]	93.6	3.7	0.7	0.69	0.41	0.25	0.18	0.01	194	0.45
Bentonite V[c)]	55.2	20.6	9.5	1.69	3.64	1.10	0.56	1.26	92	0.16
γ-Al_2O_3	tr.[e)]	99	0.01	0.0	0.0	0.01	0.0	0.0	184	0.53

a) Surface area. b) Pore volume. c) For details refer to the text. d) Bentonite S after acid treatment. e) Less than 0.5.

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Table 2. Catalytic activities for HC, HDS, and HY

Run	Support	HC of DPM				HDS of DBT		HY of 1-MN
		Conv./%[a]	HC/%[b]	HY/%[c]	Others/%[d]	HDS/%[e]	HY/%[f]	HY/%[g]
1	MoS_2/Al_2O_3	1.9	1.3	0.6	0	8.8	6.7	41.5
2	MoS_2/Bentonite AS	84.1	83.3	0	1.1	37.8	5.6	16.6
3	MoS_2/Bentonite AV	43.8	43.2	0	0.6	7.1	6.1	—
4	MoS_2/Bentonite S	30.0	21.8	0	8.2	6.0	1.2	—
5	MoO_3/Al_2O_3	0.3	0.3	0	0	13.5	3.1	18.5
6	MoO_3/Bentonite AS	80.0	78.4	0	1.6	34.7	1.5	7.0
7	MoO_3/Bentonite AV	44.1	37.2	0	6.9	9.1	0	—
8	γ-Al_2O_3	0	0	0	0	0	0	0
9	Bentonite AS	81.9	73.6	0	8.3	0	0	0.2
10	Bentonite AV	42.6	33.8	0	8.8	0	0	—

a) Total conversion. b) Yields of benzene and toluene. c) Yields of cyclohexylphenylmethane. d) Mainly polymerized products. e) Yields of biphenyl. f) Yields of cyclohexylbenzene, bicyclohexyl and tetrahydrodibenzothiophene. g) Yields of 1-methyltetralin and 5-methyltetralin.

Acid treated Bentonite S was the most effective to achieve maximum hydrocracking and HDS activities. In contrast to these results, presulfided molybdenum catalyst supported on γ-Al_2O_3 showed the highest hydrogenation activity.

Runs 5—7 shows the results obtained on oxide catalysts. Similar trends were observed for hydrocracking and hydrogenation in the case of MoO_3 supported catalyst. Higher hydrocracking and HDS activities were given on the bentonite supports. While, higher hydrogenation activity was obtained on the Al_2O_3 support, though hydrogenation activities of the oxide catalyst were lower than those of the sulfided catalyst. HDS activity obtained on MoO_3/Al_2O_3 catalyst was higher than that on MoS_2/Al_2O_3 catalyst. This may be due to the sulfiding of MoO_3. XPS analyses showed that after HDS reactions, MoO_3 changed to MoS_2 to some extent.

Large differences in hydrocracking activities were also obtained for the reactions over the support. The bentonites were found to contribute to hydrocracking activity by itself, as shown in Runs 8—10. This is the most evident in the results obtained in the present work, where the bentonite-supported catalysts gave high hydrocracking performances, in line with the known high activities of these protonic acid supports for cracking reactions.[4] Almost no hydrogenation activity was observed on the Al_2O_3 and the bentonite supports.

From these results it is considered that the role of molybdenum ions in bentonite-supported molybdenum catalyst is to give the activities for HDS and hydrogenation. Molybdenum ions also seem to improve the selectivity of the catalysts, because polymerization products decreased after impregnating MoO_3 on the bentonite. On the other hand, presulfurization seems to enhance hydrogenation activities of the catalysts, by comparing Run 2 with Run 6. In the case of the alumina-supported molybdenum catalyst, molybdenum ions gave the hydrocracking activity as well as HDS and hydrogenation activities. The presulfurization was found to contribute to the enhancement of the hydrogenation activity.

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