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Hydrodesulfurization of dibenzothiophene on alumina-supported molybdenum nitride

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An alumina-supported molybdenum nitrided catalyst was prepared and tested to determine its activity and selectivity during the hydrodesulfurization of dibenzothiophene. The nitrided catalyst was extremely active for the selective C–S bond breakage of dibenzothiophene to produce biphenyl.

Keywords: HDS; dibenzothiophene; molybdenum nitride; high selectivity

It is well known that molybdenum compounds catalyze the petroleum hydrodesulfurization (HDS) process by acting as an active catalyst. Molybdenum nitride is an active catalyst for various reactions that emulate the catalytic properties of noble metals. The reactions studied have included NH_3 synthesis [1], CO hydrogenation and C_2H_6 hydrogenolysis [2], acetonitrile hydrogenation [3], and quinoline hydrodenitrogenation [4]. Recently, Markel and Van Zee [5] reported the preparation of the unsupported Mo_2N catalyst with a high surface area for resistance against sulfiding during thiophene HDS in a catalytic reactor. During the reaction, butene was primarily formed from the C–S bond breakage of tetrahydrothiophene through the hydrogenation of thiophene, not from the direct desulfurization of thiophene during the first stage. This result indicated that the unsupported molybdenum nitride powder promoted more hydrogenation than desulfurization. However, little attention has been paid to the catalytic properties of molybdenum nitrides supported on high surface area alumina instead of unsupported γ-Mo_2N powder for industrial applications. This paper first reports that the alumina-supported molybdenum nitride catalyst is very active for the HDS of dibenzothiophene with highly selective C–S bond breakage of dibenzothiophene at 553–633 K, compared to a sulfided catalyst.

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The 11.7% molybdena on a supported alumina catalyst (Nikki Chemical Co.) was prepared using a mixture of hexaammonium molybdate and γ-alumina which was calcined in air at 823 K for 3 h. Nitriding of the catalysts was done according to the procedures of Volpe and Boudart [6]. The fresh molybdena alumina-supported catalyst (2.0 g, 10–20 mesh), packed in a reactor, was first preheated at 723 K in air and then cooled to 573 K. The catalyst was treated with pure NH_3 at 4 ℓ/h from 573 to 773 K at 1 K/min and held at 573 K for 3 h, or from 573 to 973 K at 1 K/min and held at 973 K for 3 h. To compare the catalytic property of the nitrided catalyst with the sulfided catalyst, the sulfidation of the fresh catalyst preheated at 723 K was performed in flowing 10% H_2S/H_2 at 673 K for 3 h after a 3 h reduction in H_2. The activity measurement for dibenzothiophene HDS was carried out in the high-pressure stainless-steel flow system, fixed-bed microreactor at 553–633 K and 10.1 MPa total pressure. The reaction feed, consisting of 0.25 wt% dibenzothiophene in xylene, was introduced at a rate of 20 ml/h into the reactor with a H_2 flow of 6 ℓ/h. The surface composition of the nitrided Mo/Al_2O_3 catalyst was measured using XPS and elemental analysis before and after the reaction.

The nitrogen content and the BET surface area of the nitrided catalysts are shown in table 1. The nitrogen content of the 773 K nitrided catalyst was 2.5 times the stoichiometric value when the nitrided catalyst was evacuated at 10^{-4} Torr at 473 K before measurement of the nitrogen content of the catalyst. The nitrogen content of the nitrided catalyst decreased with increasing evacuation temperature and attained the stoichiometric value (0.6 wt%) at 773 K. For the 973 K nitrided catalyst, the nitrogen content approached the values of 0.5 wt% nitrogen when the evacuation temperature was increased to 973 K. It was found that the catalyst nitrided at a higher temperature had a higher nitrogen content in the catalyst. Furthermore, the surface area of the 773 K nitrided catalyst decreased with increasing evacuation temperature. It is still not clear why the surface is significantly decreased by evacuation at higher temperature: since the nitrided Mo/Al_2O_3 cata-

Table 1
The composition of the nitrided 11.7% Mo/Al_2O_3

Nitridation (NH_3 flow rate)	Evacuation temp. (K)	Nitrogen content (wt%)	Nitrogen ratio[a]	BET (m^2/g)
773	473	1.5	2.5	268.9
	673	0.6	1.0	–
	773	0.6	1.0	152.1
973	473	1.6	2.7	195.4
	673	1.0	1.7	–
	773	0.8	1.3	–
	973	0.5	0.8	–

[a] The value is the ratio of the nitrogen content to stoichiometric nitrogen content (0.6 wt%) of the 11.7% Mo_2N/Al_2O_3 catalyst.

lyst retained a significant amount of adsorbed NH_3 on the surface at 473 K, ammonia probably interrupted N_2 adsorption onto the surface of the catalyst. The treatment of the nitrided catalyst at evacuation temperatures higher than 673 K can remove large amounts of ammonia adsorbed on the catalyst. Furthermore, the surface area of the catalyst evacuated at 773 K decreased from 268.9 m^2/g for the catalyst evacuated at 473 K to 152.1 m^2/g.

The effect of residence time on conversion and selectivity is shown in fig. 1. The major product was biphenyl with a small amount of cyclohexylbenzene in dibenzothiophene HDS on the 773 K nitrided catalyst. A very small amount of bicyclohexyl and tetrahydrodibenzothiophene was also produced. The formation of biphenyl, cyclohexylbenzene, and bicyclohexyl increased with increasing residence time, while both dibenzothiophene and tetrahydrodibenzothiophene decreased with increasing residence time. From the results, tetrahydrodibenzothiophene is an intermediate compound, while biphenyl, cyclohexylbenzene, and bicyclohexyl are the final desulfurized compounds. The effect of biphenyl addition on dibenzothiophene HDS was studied in order to determine whether biphenyl was hydrogenated to form cyclohexylbenzene in the presence of the nitrided catalyst (fig. 2). When 0.11 wt% biphenyl was added to the 0.25 wt% dibenzothiophene in xylene at 573 K,

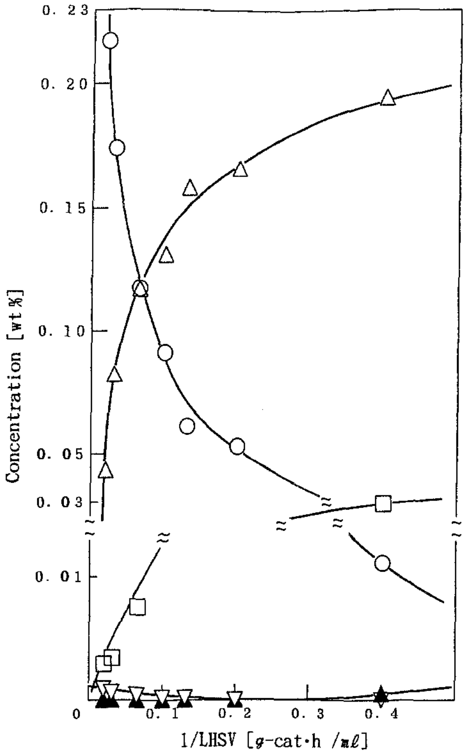

Fig. 1. The reaction products as a function of residence time (1/LHSV) in the feed ($T = 573$ K, $W = 0.65$–2.0 g); (○) dibenzothiophene; (△) biphenyl; (□) cyclohexylbenzene; (▽) tetrahydrodibenzothiophene; (▲) bicyclohexyl.

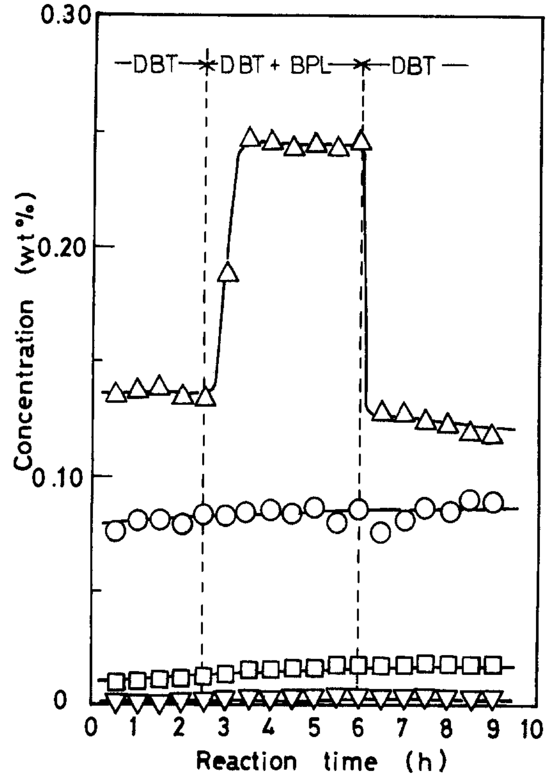

Fig. 2. The effect of the addition of biphenyl on dibenzothiophene HDS at 573 K. For the symbols see fig. 1. DBT: dibenzothiophene; BPL: biphenyl.

the amount of biphenyl was increased by the same amount of biphenyl added. No cyclohexylbenzene increased during the period of biphenyl addition. This result shows that biphenyl is not hydrogenated to form cyclohexylbenzene at 573 K. Moreover, since neither perhydrodibenzothiophene nor bicyclohexyl were detected in the HDS, the nitrided catalyst facilitated no deep hydrogenation of dibenzothiophene through perhydrodibenzothiophene to form bicyclohexyl [7] as shown in fig. 2. In the dibenzothiophene-HDS network, hydrogenation as well as S-removal reactions are present as shown in fig. 3. This reaction takes place via the direct hydrogenolysis of dibenzothiophene to biphenyl or via hydrogenation of dibenzothiophene followed by S removal. This reaction scheme is in agreement with the one proposed by Nagai et al. [7].

The dependence of the partial pressure of hydrogen and dibenzothiophene on the conversion of dibenzothiophene at 583 K is shown in fig. 4. The conversion of dibenzothiophene at 6.0 MPa hydrogen pressure (P_H) was only increased by 10% more than at 1.6 MPa hydrogen pressure. The conversion was 0.1 order with respect to hydrogen pressure. Moreover, the concentration of biphenyl was nearly constant notwithstanding the increase in hydrogen partial pressure. These results

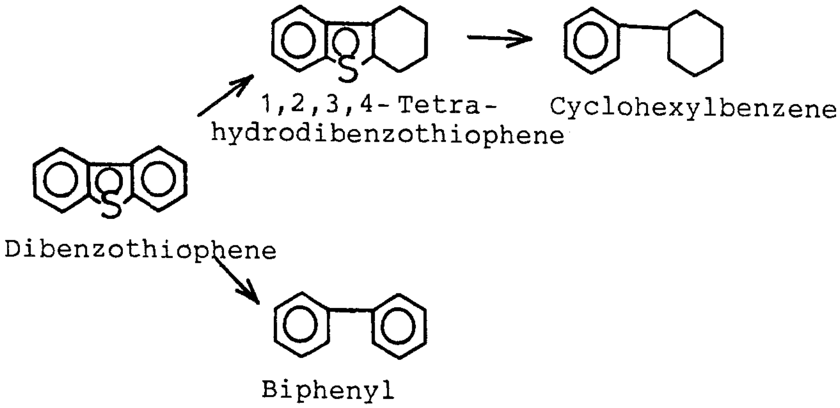

Fig. 3. The reaction network of the HDS of dibenzothiophene.

suggested that the nitrided catalyst was active for the highly selective sulfur removal even at lower hydrogen pressure. However, the conversion decreased by 15% when the dibenzothiophene concentration was increased from 0.02 to 0.41 wt%. Therefore, the power law rate equation (r_{conv}) for dibenzothiophene HDS on the nitrided catalyst at 573 K and 10.1 MPa total pressure, is given by

$$r_{\mathrm{conv}} = kP_{\mathrm{H}}^{0.1} P_{\mathrm{D}}^{-0.1} ,$$

where r_{conv} is the rate of the conversion of dibenzothiophene, and P_{H} and P_{D} are partial pressure of hydrogen and dibenzothiophene, respectively.

The activity and selectivity of the nitrided and sulfided Mo/Al_2O_3 catalyst for dibenzothiophene HDS, compared with those of the sulfided catalyst are shown in table 2. The conversion of dibenzothiophene on the 773 K nitrided catalyst was 38% at 553 K, but that on the sulfided catalyst was 29%. The nitrided catalyst is 1.2

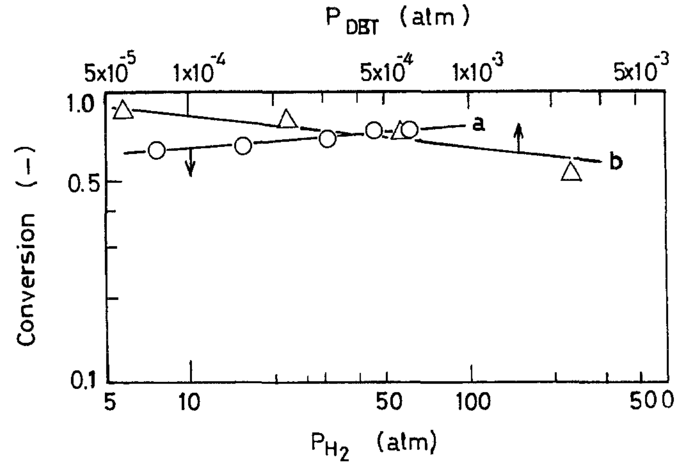

Fig. 4. The dependence of hydrogen partial pressure (a) and dibenzothiophene (b) on the activity of the 11.7% Mo/Al_2O_3 nitrided catalyst in dibenzothiophene HDS.

Table 2
The HDS activity and selectivity of the Mo/Al_2O_3 catalysts

Catalyst pretreatment	Reaction temp. (K)	Conversion (%)	Biphenyl (wt%)	Cyclohexylbenzene (wt%)	HDS selectivity[a]
nitrided[b]	553	38	0.059	5×10^{-4}	118
	593	72	0.149	0.006	25
	633	90	0.178	0.0135	13
sulfided[c]	553	29	0.047	0.036	1.3
	593	59	0.099	0.048	2.1
	633	83	0.153	0.05	3.1

[a] The HDS selectivity represents the molar ratio of biphenyl/cyclohexylbenzene.

[b] BET surface area of 267.2 m^2/g, Mo/N ratio= 1.0. The catalyst was evacuated at 10^{-4} Torr and 773 K before measurement of the nitrogen content of the catalyst.

[c] The catalyst was sulfided in flowing 10% H_2S/H_2 at 673 K for 3 h.

and 1.1 times more active than the sulfided catalyst at 553 and 633 K, respectively. The index of the selectivity of the catalyst for desulfurization to hydrogenation is evaluated by the molar ratio of biphenyl to cyclohexylbenzene in table 2. The selectivity of the nitrided catalyst for the selective desulfurization is 91 and 12 times more than that of the sulfided catalyst at 553 and 593 K, respectively. It was found that the nitrided catalyst was significantly active toward direct sulfur removal from dibenzothiophene with less consumption of hydrogen.

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