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Hydrodesulfurization of Dibenzothiophene on Nitrided Mo/Al_2O_3 Catalysts

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Abstract

The relationship between the HDS activity and the surface properties of alumina-supported molybdenum nitride catalysts was studied. The 500°C- and 700°C-nitrided 12·5% Mo/Al_2O_3 catalysts contained nitrogen amounts of 0·200 and 0·386 mmol g-cat^{-1}, respectively, when evacuated at 700°C. Nitrogen is difficult to remove from these catalysts after the nitriding treatment at high temperature. The molybdenum nitride catalyst exhibited a very active catalyst for the HDS of dibenzothiophene with a highly selective C–S bond breakage of dibenzothiophene at 280–360°C, compared with the sulfided catalyst. The nitrided 12·5% MoO_3/Al_2O_3 catalysts have broad peaks of Mo $3p_{3/2}$, Mo3d and N 1s binding energies. The decreasing activity of the catalyst was attributed to the formation of Mo sulfide and sulfur powder on the surface. The Mo species on the surface and the active sites of the nitride catalyst for the HDS of dibenzothiophene were discussed. © *1997 Elsevier Science Limited.*

1 Introduction

It is well known that molybdenum compounds catalyze the petroleum hydrodesulfurization (HDS) process by acting as active catalyst. An increasing interest has developed in exploring the catalytic properties of transition metal nitrides, such as Mo_2N and W_2N. Molybdenum nitride is an active catalyst to compete with the catalytic properties of noble metals. Recently, Markel and Van Zee[1] studied the preparation of the unsupported Mo_2N powder catalyst for resistance against sulfiding during the HDS of thiophene. In the reaction, butene was primarily formed from the C–S bond breakage of tetrahydrothiophene through the hydrogenation of thiophene during the first stage of the reaction. This result indicated that the unsupported Mo_2N powder promoted more hydrogenation than desulfurization. We reported, however, that nitridation enhanced the activity and selectivity of the Mo/Al_2O_3 catalysts for the direct desulfurization of dibenzothiophene to form biphenyl, compared with the sulfided catalyst.[2] In this study, the effects of nitriding conditions on the activity and selectivity of the nitrided Mo/Al_2O_3 catalysts for the HDS of dibenzothiophene were determined. The relationship between the surface properties and the HDS activity of the nitrided catalysts was discussed.

2 Experimental

A 12·5% MoO_3/Al_2O_3 was prepared using a mixture of ammonium paramolybdate and alumina xerogels. The solid was crashed and mixed with alumina hydrogel. The gel was calcined at 550°C for 3 h to form the Al_2O_3-supported MoO_3. Nitriding of the catalysts was done according to the procedures of Volpe and Boudart.[3] The 12·5% MoO_3/Al_2O_3 was treated with pure NH_3 at 4 l h^{-1} from 300–500, 700, and 900°C at 1°C min^{-1}, held at this temperature for 3 h, and then cooled to room temperature in flowing NH_3. The nitrided catalyst was passivated in 1% O_2/He for 12 h for measurement of the catalyst activity. For sulfidation, the fresh catalyst was sulfided *in situ* in a stream of 10% H_2S/H_2 at 350 and 500°C for 3 h. The activity measurement for dibenzothiophene HDS was carried out using a fixed-bed microreactor at 280–360°C and 10·1 MPa total pressure. The reaction feed, consisting of 0·25 wt% dibenzothiophene in xylene, was introduced into the reactor at a rate of 20 ml h^{-1} with H_2 flow of 6 l h^{-1}. The surface composition and property of the nitrided

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Mo/Al_2O_3 catalysts were measured using CHN analyzer, atomic absorption, and XPS spectroscopies.

3 Results and Discussion

3.1 Surface area and nitrogen content

The surface area and nitrogen content of the catalysts are shown in Table 1. Nitriding of the 12·5% MoO_3/Al_2O_3 at 500°C decreased the surface area by only less than 8%. Surface area of $226\,m^2\,g^{-1}$ was confirmed for the 500°C-nitrided catalyst, although it was $245\,m^2\,g^{-1}$ in its fresh state. The surface area of the catalyst decreased $31\,m^2\,g^{-1}$ when the nitriding temperature was increased from 500 to 700°C. Nitriding in flowing NH_3 at 900°C decreased the surface area significantly. The surface area of the 900°C-nitrided catalyst decreased to 61% of that of the 500°C-nitrided catalyst.

The nitrogen in the amounts of 0·200 and 0·386 mmol g-cat^{-1} contained in the 12·5% 500°C- and 700°C-nitrided catalysts, respectively, evacuated at 700°C. The amount of 0·386 mmol g-cat^{-1} (12·5%Mo/Al_2O_3) corresponded to 3·10 mmol g^{-1} of N, when converted to the desorption amount for 100% MoO_2. Hillis *et al.*[4] reported that little chemisorption of N_2 occurred with pure MoO_2, in the temperature range of 0 to 550°C, but reduced Mo dioxide readily adsorbed nitrogen, forming a nitride. The nitrogen amount of 3·10 mmol g^{-1}-MoO_2 is greater than 2·67 mmol g^{-1}-MoO_2 obtained by Balandin and Rozhdestvenskaya,[5] suggesting that much nitrogen was adsorbed by alumina treated with NH_3 at 500°C. Nitrogen was adsorbed in the 700°C-nitrided catalyst by 0·093 mmol g^{-1} of N greater than on the 500°C-nitrided catalyst. This result provided evidence that nitrogen is difficult to remove from these catalysts after the nitriding treatment at high temperature, even if they were evacuated at 700°C. It appears that a nitrogen atom was bonded to an Mo atom to form an Mo nitride for the Mo/Al_2O_3 catalyst nitrided in severe conditions. Therefore, excess nitrogen of the catalysts was probably presented as physically or chemically adsorbed NH_3 and N on the catalyst, or even as dissolved N in it.[6,7]

Table 1. Surface area and nitrogen content of the catalysts

Catalyst[a]	*Surface area*[e] *($m^2\,g^{-1}$)*	*N content*[f] *(mmol g^{-1})*	*N/Mo Atomic ratio*[g]
Nitrided at 500°C[b]	226	0·200	0·24
Nitrided at 700°C[c]	195	0·421	0·46
Nitrided at 900°C[d]	138	0·386	0·35

[a] The catalysts were nitrided in flowing NH_3 from 350 to
[b] 500°C
[c] 700°C
[d] 900°C at a rate of 1°C min^{-1} and 0·1 MPa and held at this temperature for 3 h.
[e] The surface area of fresh 12·5% MoO_3/Al_2O_3 catalyst was $245\,m^2g^{-1}$.
[f] Nitrogen content was measured using a Perkin-Elmer CHN elemental analyzer (oxygen burning method). The catalyst was evacuated at 700°C.
[g] The Mo loading was 12·5% Mo in the sample (evacuated at 700°C) measured by atomic adsorption.

3.2 HDS activity

The effect of residence time on conversion and selectivity is shown in Fig. 1. The major product was biphenyl along with a small amount of cyclohexylbenzene in the HDS of dibenzothiophene on the nitrided catalyst. 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.

In the dibenzothiophene-HDS network, hydrogenation as well as S-removal reactions are present as shown in this scheme (Fig. 2). This reaction

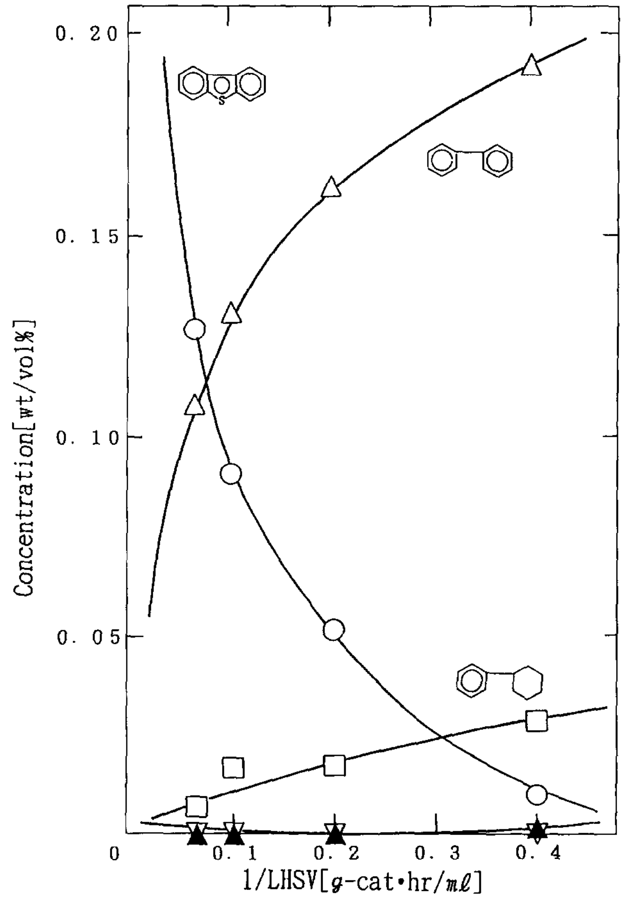

Fig. 1. The effect of residence time on conversion in the HDS of dibenzothiophene on nitrided and sulfided 12·5% MoO_3/Al_2O_3. ○ dibenzothiophene, ▽ tetrahydrodibenzothiophene, △ biphenyl, □ cyclohexylbenzene, ▲ bicyclohexyl.

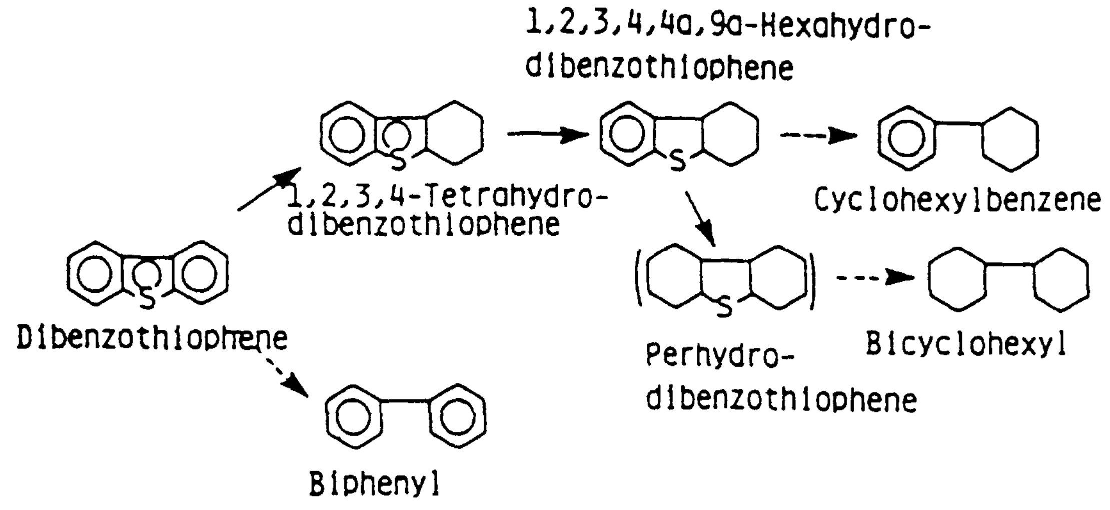

Fig. 2. Reaction scheme for the HDS of dibenzothiophene.

takes place via the direct hydrogenolysis of dibenzothiophene to biphenyl or via hydrogenation of dibenzothiophene followed by S-removal. The former product was formed by the direct sulfur removal from dibenzothiophene, and the latter from the hydrogenation of dibenzothiophene through hexahydrodibenzothiophene.

The HDS rate of the nitrided and sulfided catalysts for the HDS of dibenzothiophene at 300°C is shown in Table 2. For the catalyst activity (per unit of gram), the nitrided catalysts in various nitriding conditions were more active than the 500°C-sulfided catalyst. The activity of the 500°C-nitrided catalyst was the highest, while that of the 350°C-sulfided catalyst was second. The nitriding treatment at higher temperature decreased the activity of the Mo/Al_2O_3 catalyst for the HDS of dibenzothiophene. The selectivity of the catalyst for desulfurization to hydrogenation is evaluated by the molar ratio of biphenyl to cyclohexylbenzene, and shown in Table 2. The selectivity of the 500°C-nitrided catalyst for the direct desulfurization is 3·1 times more than that of the 350°C-sulfided catalyst.

The nitrided catalyst was extremely active for the selective C–S bond breakage of dibenzothiophene to produce biphenyl. From these results, the nitrided catalyst was significantly active toward direct sulfur removal from dibenzothiophene with less consumption of hydrogen.

3.3 XPS Analysis — Mo species on the surface

The surface composition of the nitrided molybdenum catalysts was investigated using X-ray photoelectron spectroscopy. N ls and Mo $3p_{3/2}$ XPS spectra for the fresh and nitrided 12·5% MoO_3/Al_2O_3 catalysts evacuated at 200°C are shown in Fig. 3. The XPS data for the Mo_2N powder (Nilaco Co.) are also shown for comparison. The Mo_2N powder has two sharp binding energies, one at 397·4 eV (N ls binding energy for Mo–N) and the other at 394·0 eV (Mo $3p_{3/2}$ for Mo–N), whereas the nitrided 12·5% MoO_3/Al_2O_3 catalysts have broad Mo $3p_{3/2}$ binding energies as well as small peaks for the N 1s lines. The measured Mo $3p_{3/2}$ spectral envelope overlapped the N 1s spectra and contained spectra of several molybdenum states: Mo^{6+} (399·4 eV), Mo^{5+} (398·3 eV), Mo^{4+} (396·3 eV), and Mo^0 (393·6 eV).[8,9] A small Mo $3p_{3/2}$ binding energy of 393·6 eV was observed for the 900°C-nitrided catalyst. The small peaks of the N ls lines at 397·4, 398·8, and 399·7 eV were observed for the nitrided 12·5% MoO_3/Al_2O_3 catalysts. The N 1s binding energy at 397·4 eV is characteristic of an Mo–N nitride.[10] The second and third peaks at 398·8 and 399·7 eV were reported assigned to the N 1s levels of NH_3 adsorbed on the surface Lewis sites and Bronsted acid sites, respectively.[11] Although it appeared that NH_3 treatment at more than 500°C brought about the formation of

Table 2. Catalyst activity for HDS of dibenzothiophene

Catalyst	*HDS rate*[a] (μ mol g^{-1} h^{-1})	(μ mol m^2 h^{-1})	*Biphenyl/ cyclohexylbenzene*
Nitrided at 500°C	97·6	0·432	4·7
Nitrided at 700°C	66·6	0·342	4·3
Nitrided at 900°C	60·8	0·441	7·2
Sulfided at 500°C[b]	42·1	0·199	1·7
Sulfided at 300°C[c]	81·5	0·347	1·5

[a] HDS activity is based on the rate for disappearance of dibenzothiophene.

[b,c] The surface areas of the sulfided catalysts at 500°C and 300°C are 212 m^2 g^{-1} and 235 m^2 g^{-1}, respectively.

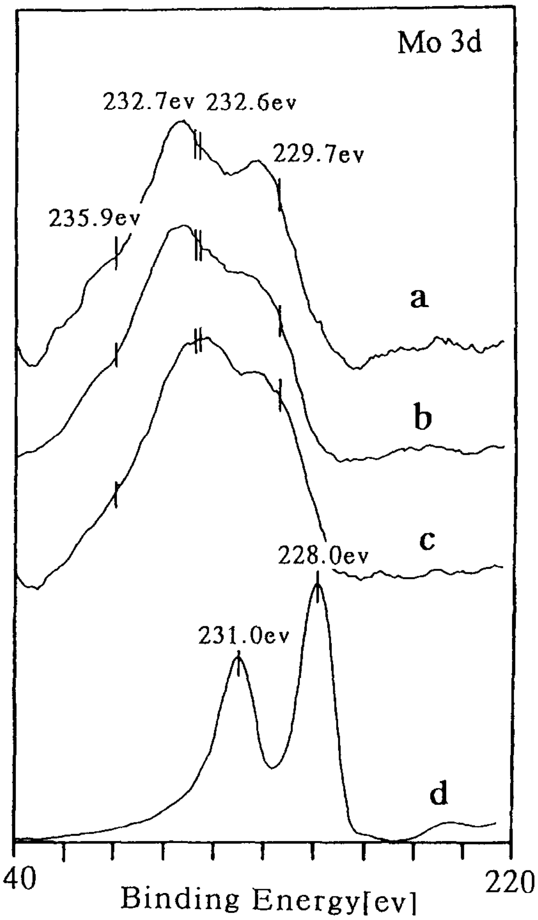

Fig. 3. The binding energies of the Mo $3d_{5/2}$ and $3d_{3/2}$ for the (a) 500°C-, (b) 700°C-, and (c) 900°C-nitrided catalysts and (d) Mo_2N sample.

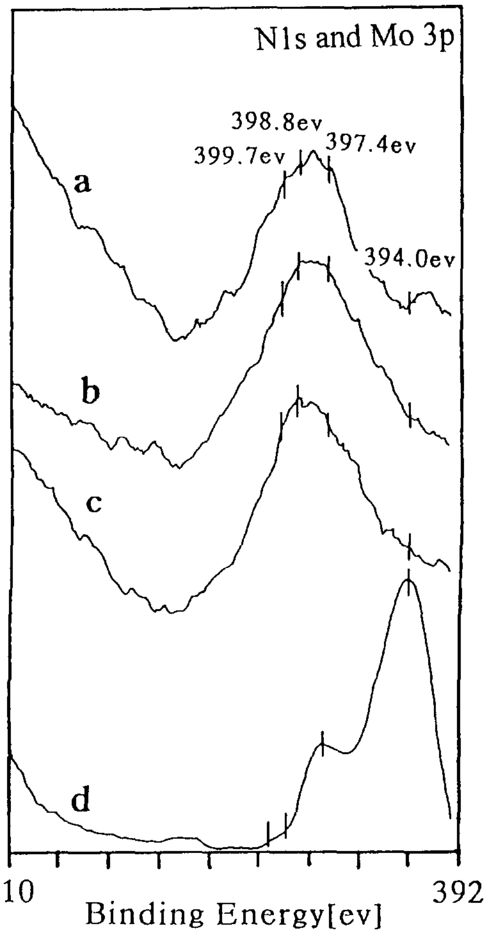

Fig. 4. The XPS binding energies of N 1s and Mo 3p for the (a) 500°C-, (b) 700°C-, and (c) 900°C-nitrided catalysts and (d) Mo_2N sample.

nitrides (Mo–N) on the surface of the 12·5% MoO_3/Al_2O_3 catalyst, the peaks found could not be related with the nitrides nor nitrogen compounds adsorbed, because the XPS peak of Mo 2p was overlapped with that of N 1s for the nitrided Mo/Al_2O_3 catalyst.

The binding energies of the Mo $3d_{5/2}$ and $3d_{3/2}$ for the Mo_2N powder and the 12·5% MoO_3/Al_2O_3 catalysts nitrided under various conditions are shown in Fig. 4. The Mo 3d peaks were broad for the nitrided 12·5% MoO_3/Al_2O_3 catalysts after NH_3 treatment, whereas they were very sharp for the Mo_2N powder with the Mo $3d_{5/2}$ binding energy at 228·0 eV. The peaks for the four nitrided catalysts were shifted to a binding energy higher than 229·7 eV. Note that the Mo $3d_{5/2}$ binding energy of higher than 229·7 eV is between the binding energies for Mo^{5+} (231·4 eV), Mo^{4+} (229·6 eV), and Mo^{3+} (228·8 eV).[12,13] The XPS data for the nitrided 12·5% MoO_3/Al_2O_3 catalysts indicated that molybdenum species on the catalysts were likely to be widely distributed from Mo^{3+} to Mo^{5+}.

The S2p XPS spectra for the 500°C-nitrided catalysts before and after the reaction were evaluated to determine the deactivation of the nitrided catalyst. Sulfur content of the nitrided catalysts after the reaction was estimated by the XPS S 2p peak. The 500°C-nitrided catalyst after reaction was sulfided to a degree of 23% of the 350°C-sulfided catalyst. However, the sulfidation for the 500°C-nitrided catalyst, which was sulfided at 350°C after nitriding, was increased to 43% of the sulfided catalyst. The nitrided catalyst was apparently tolerant to sulfidation during the reaction, comparing to sulfiding treatment in a 10% H_2S/H_2 stream. The binding energies of S2p for the nitrided catalysts after the reaction were observed at 163·8 and 162·4 eV. The S2p XP spectrum for the sulfided catalyst was observed at the 163·0 eV peak, but the spectra for the nitrided catalyst, which was sulfided after nitriding, were observed at 164·4 and 163·2 eV. The peaks at 164·4 and 163·0 eV were ascribed to sulfur species, S^0 and S^{2-}, respectively. The XPS data showed that the surface of the spent catalyst was covered with sulfur powder (S^0) and sulfur ions of MoS_2 (S^{2-}) The formation of MoS^2 during the reaction led to a decrease in the activity of the nitrided catalyst to approach that of the sulfided catalyst. This decreasing activity of the catalyst was attributed to the structure changes associated with sulfur depletion.

4 Conclusions

1. The activity of the 500°C-nitrided catalyst was the highest, the 350°C-sulfided catalyst second. The HDS activity of the Mo/Al_2O_3 catalysts decreased with increasing nitriding temperature.
2. The Mo nitride catalyst was extremely active for the selective C–S bond breakage of dibenzothiophene to produce biphenyl. The HDS of dibenzothiphene takes place via the direct C–S hydrogenolysis of dibenzothiophene and via hydrogenation of dibenzothiophene followed by S-removal.
3. Excess nitrogen was present on the catalyst as physically or chemically adsorbed NH_3 and N, or even as dissolved N. Nitrogen is difficult to remove from the catalysts after the nitriding treatment at high temperature, even though the catalysts were evacuated at 700°C.
4. The XPS data indicated that molybdenum species on the nitrided catalysts were likely to be widely distributed from Mo^{3+} to Mo^{5+}.

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