Preparation of Mo Nitride Catalysts and Their Applications to the Hydrotreating of Indole and Benzothiophene

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Abstract—Molybdenum nitrides were prepared by temperature-programmed reduction of MoO_3 with flowing NH_3. They were tested for indole HDN and benzothiophene HDS. Too low or high NH_3 space velocity was inadequate to produce high surface area Mo nitride. The temperature ramping rate (except the rate higher than 2.5 K/min in β1 temperature range) hardly affected the surface area of the prepared samples. The XRD analysis suggested that MoO_2 was the important intermediate for producing the high surface area Mo nitride. The catalytic conversions of Mo nitrides for indole HDN and benzothiophene HDS were well correlated with their surface areas. The reaction pathways of both reactions were proposed. The Mo nitride could be an effective catalyst without further hydrogenation of aromatics, thereby reducing the consumption of hydrogen.

Key words: Mo Nitride, Indole HDN, Benzothiophene HDS, TPR with NH_3, Mo Oxynitride

INTRODUCTION

Molybdenum nitride has shown promise as a catalyst in the areas of ammonia synthesis, quinoline hydrodenitrogenation (HDN), thiophene hydrodesulfurization (HDS), CO hydrogenation and ethane hydrogenolysis [Volpe et al., 1983, 1986; Ranhotra et al., 1987; Schlatter et al., 1988; Markel et al., 1990; Oyama, 1992]. Particularly, Mo_2N had an activity for quinoline HDN comparable to that of a currently available commercial $NiMo/Al_2O_3$ catalyst, and showed better selectivity toward C-N bond activation [Choi et al., 1992]. Also, an alumina-supported Mo_2N catalyst was extremely active for the selective C-S bond breakage of dibenzothiophene to produce biphenyl [Nagai et al., 1993; Colling et al., 1994].

Molybdenum nitride prepared by the classical high-temperature synthesis route has very low surface area, typically less than 1 m^2/g [Toth, 1971]. The reaction of MoO_3 with ammonia, however, can produce Mo_2N with a surface area even in excess of 200 m^2/g [Volpe et al., 1983]. The reaction is known as a topotactic transformation with conservation of the two-dimensional layers of the oxide precursor in the nitride product [Volpe et al., 1983, 1986]. Molybdenum trioxide forms two intermediates of MoO_2 and Mo oxynitride in its reactions with ammonia to form molybdenum nitride [Choi et al., 1994; Jaggers et al., 1990; Wise et al., 1994]. However, it was not verified until now what role the intermediates play in producing high surface area Mo nitride.

The present investigation was undertaken to gain further insights into the role of the intermediates in producing high surface area Mo nitrides. X-ray diffraction was used to observe the formation and transformation of the intermediates during the reaction of MoO_3

with NH_3. The prepared catalysts were then employed for indole HDN and benzothiophene HDS reaction. The pathways of both reactions are proposed.

EXPERIMENTAL

1. Preparation of Mo Nitrides

Mo nitrides were prepared by reacting MoO_3 (Aldrich, 99%) with flowing ammonia (Solkatronic Chemicals, 99.999%). Different ammonia flow rates and linear heating rates were employed to control the degree of nitridation. Procedures for the preparation of Mo nitride were adopted from the temperature-programmed reduction method of Choi et al. [Choi et al., 1994]. A 1.4 gram amount of MoO_3 powder was placed in a quartz reactor and reduced in flowing ammonia. The following reduction schedule was generally employed, unless otherwise specified. The reduction temperature was rapidly increased from room temperature to 623 K over 30 min, then increased to 723 K (β1 temperature range, 623-723 K) over 150 min, raised from 723 K to 973 K (β2 temperature range, 723-973 K) over 75 min, and finally held for 60 min at 973 K. The prepared Mo nitride was cooled to room temperature, and then passivated with 1% O_2 in He for 60 min.

2. Characterization

The crystalline structures of Mo nitrides were analyzed by using X-ray diffraction (XRD). The diffraction patterns were collected by using Rigaku DMAX-B diffractometer and CuKa radiation. The surface areas of the prepared samples were measured from N_2 adsorption.

3. Indole HDN and Benzothiophene HDS

Reactions were performed in a quartz microreactor operated at atmospheric pressure. Indole (Aldrich, 99%) and benzothiophene (Aldrich, 99%) were delivered by a syringe pump into a flow of hydrogen. Hydrogen and liquid flow rate were 120 cc/min and 0.1 cc/h, respectively. Products were passed through a heated transfer

Table 1. Catalyst code and surface area of the prepared Mo nitrides

Catalyst code	Molar hourly space velocity (SV)[a]	Surface area[b], m^2/g
T1	11.6	80
T2	23.1	84
T3	46.2	114
T4	61.7	115
T5	84.8	113
T6	123.4	76

[a]$SV = mol\ NH_3/mol\ MoO_3 \cdot h.$

[b]All surface areas were obtained after passivation procedure.

line into a gas chromatograph (HP 5890 II) and analyzed with an FID detector. A polydimethylsiloxane capillary column was used and the products were identified by a GC-MS (HP 5971). For investigating the reaction pathways of benzothiophene HDS and indole HDN reaction over Mo nitrides, the reaction products were analyzed continuously, while the reaction temperature was increased from 573 K to 773 K at the rate of 10 K/min.

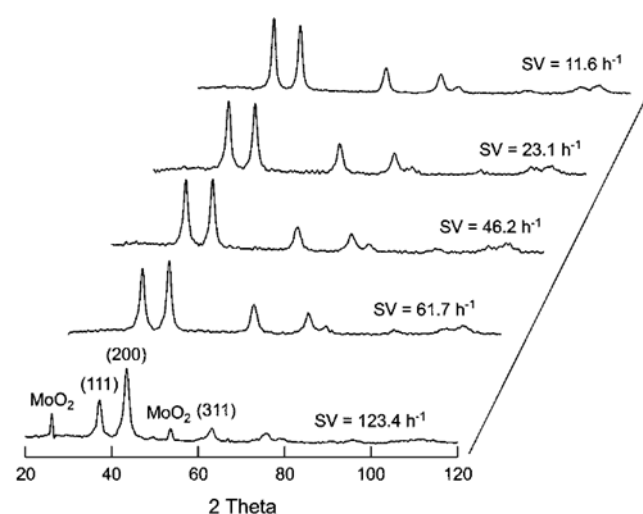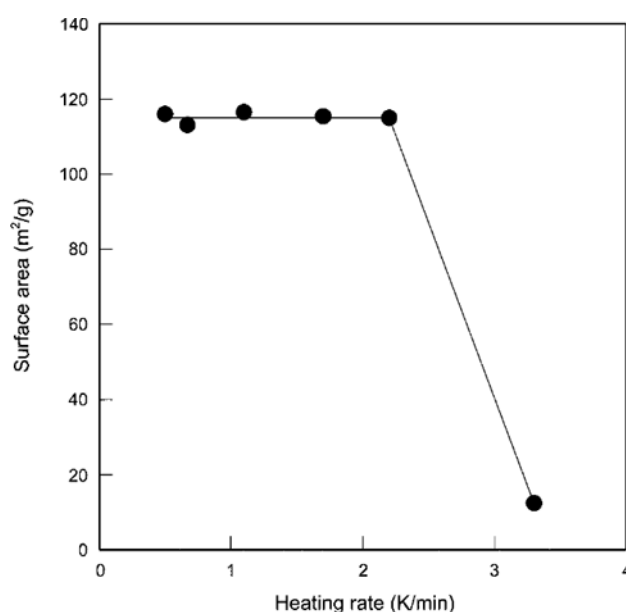## RESULTS AND DISCUSSION

1. Preparation of Mo Nitrides

Table 1 shows the surface areas of the Mo nitride catalysts prepared under different NH_3 molar hourly space velocities (SV). Surface area of the Mo nitrides was affected significantly by NH_3 molar hourly space velocity. Too low or high NH_3 molar hourly space velocity was inadequate to produce Mo nitride with high surface area; there evidently existed an optimum NH_3 space velocity to achieve the highest surface area. The lower space velocity produced higher concentrations of H_2O and may allow the accumulation of H_2O in the bed. The presence of water can limit NH_3/solid contact, and the resulting poor contact may decrease the conversion into the nitride phase. Water can also cause hydrothermal sintering. The presence of even small amounts of water is reported to cause hydrothermal

sintering by many authors [Schlatter et al., 1988; Markel et al., 1990]. When the space velocity is too high (SV=123.4 h⁻¹), the conversion of the topotactic reaction between MoO_3 and flowing NH_3 is not expected to be high enough to produce high surface area Mo nitride.

Fig. 1 shows the XRD patterns of the prepared Mo nitride catalysts at various NH_3 space velocities. Most of the catalysts showed the typical XRD patterns of Mo_2N. When Mo nitride was prepared with low NH_3 space velocity, the intensity of the (200) plane of Mo_2N was lower than that of the (111) plane. The relative intensity of the (200) plane of Mo_2N increased with NH_3 space velocity. It has been reported that the Mo nitride with intense XRD peaks of the (200) plane has high surface area [Volpe and Boudart, 1985; Jaggers et al., 1990; Markel and van Zee, 1990; Choi et al., 1992]. The increase in surface area with NH_3 molar hourly space velocity is thought to be closely related to the development of (200) plane. At much higher NH_3 molar hourly space velocity (SV=123.4 h⁻¹) the development of the (200) plane was outstanding, but MoO_2 still remained in large quantities. The remaining MoO_2 indicates that the topotactic reaction did not proceed to a full extent as mentioned above, thereby causing the decrease in surface area.

Fig. 2 shows the changes in surface area of Mo nitride when the heating rate in β1 temperature range (623 K to 723 K) was varied. Molar hourly space velocity of NH_3 was kept at 61.7 h⁻¹. The heating rate below 2.5 K/min produced high surface area, but more rapid heating rate (above 2.5 K/min) caused a sharp drop in the surface area of Mo nitride. The effect of heating rate in the β2 region (723 K to 973 K) on surface area was also investigated (Fig. 3). In this temperature region, the heating rate affected the surface area only slightly. So the heating rate below 2.5 K/min in β1 temperature range can be said to be a prerequisite for producing a high surface area Mo nitride.

In order to obtain a better understanding of the intermediates, the crystalline structure was analyzed with XRD during tempera-

Fig. 1. X-ray diffraction patterns of the prepared Mo nitride catalysts at various NH_3 molar hourly space velocities (SV).

Fig. 2. Changes in surface areas of Mo nitride with the rate of heating from 623 K to 723 K (β1 temperature range).
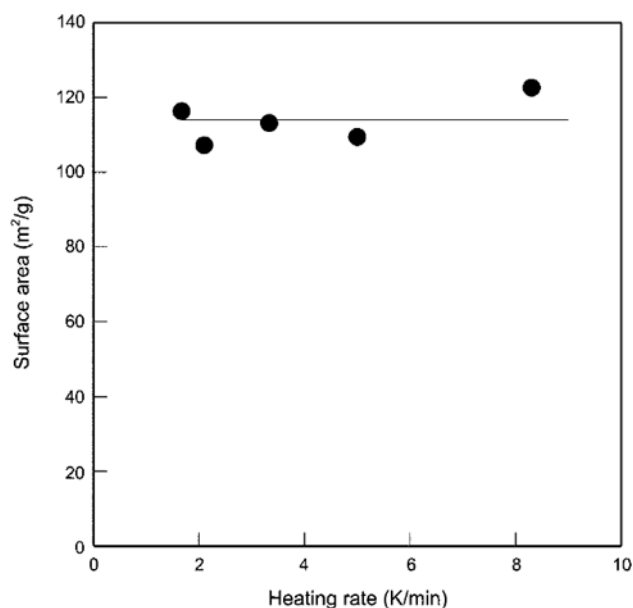
Fig. 3. Changes in surface areas of Mo nitride with the rate of heating from 723 K to 973 K (β2 temperature range).
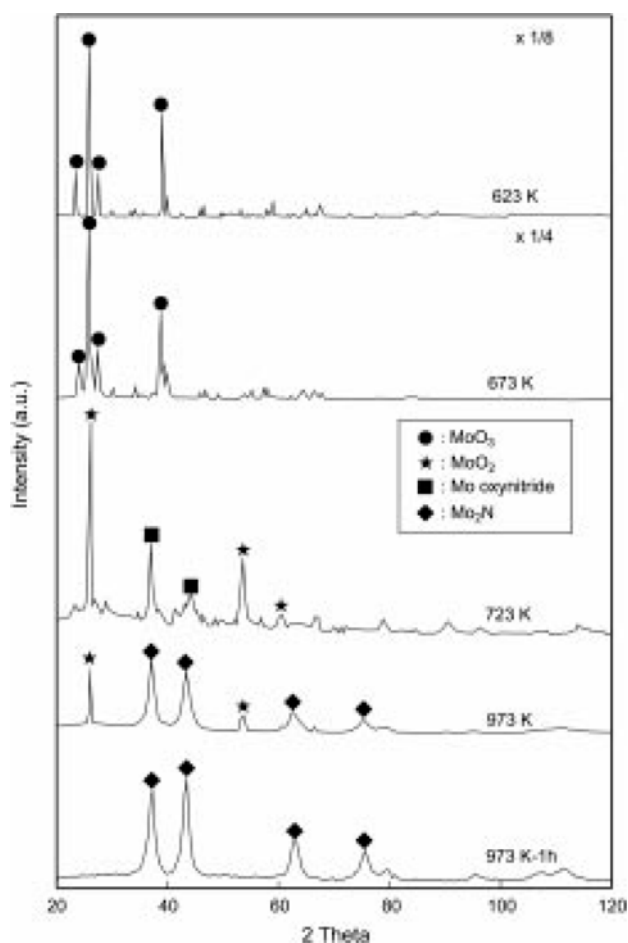
As the reduction temperature increased from 673 K to 723 K, MoO_3 transformed gradually into MoO_2 and Mo oxynitride, and at 723 K MoO_3 almost disappeared. The formation of Mo oxynitride between 673 K and 723 K is reported by many authors [Choi et al., 1994; Jaggers et al., 1990; Wise et al., 1994]. At 973 K most of the Mo oxynitride converted to Mo_2N, and MoO_2 peaks decreased greatly. When the sample was treated at 973 K for an additional 1 h, MoO_2 transformed into Mo_2N, especially into the (200) plane of Mo_2N. From the above results, we conclude that MoO_3 reduction with flowing NH_3 proceeds via the formation of both the MoO_2 and Mo oxynitride intermediates to Mo_2N. Further studies are, however, needed to elucidate the role of each intermediate on the production of high surface area Mo_2N. To do this separate XRD patterns were measured at the end of the temperature programming to 973 K and after holding the sample at 973 K for another hour (Fig. 5). When the NH_3 space velocity was low, the MoO_2 peak was very weak and no detectable change in Mo_2N peak intensity was observed even after being held for an additional hour. In the case of Mo nitride prepared under moderate NH_3 space velocity, MoO_2 phase transformed into Mo_2N phase, especially into the (200) phase. This transformation into the (200) plane became more evident from the Mo nitride prepared under high NH_3 space velocity. These results mean that during the reduction of MoO_3 with NH_3, MoO_2 plays an im-

Fig. 4. XRD patterns of T4 catalyst during temperature-programmed reduction with ammonia.
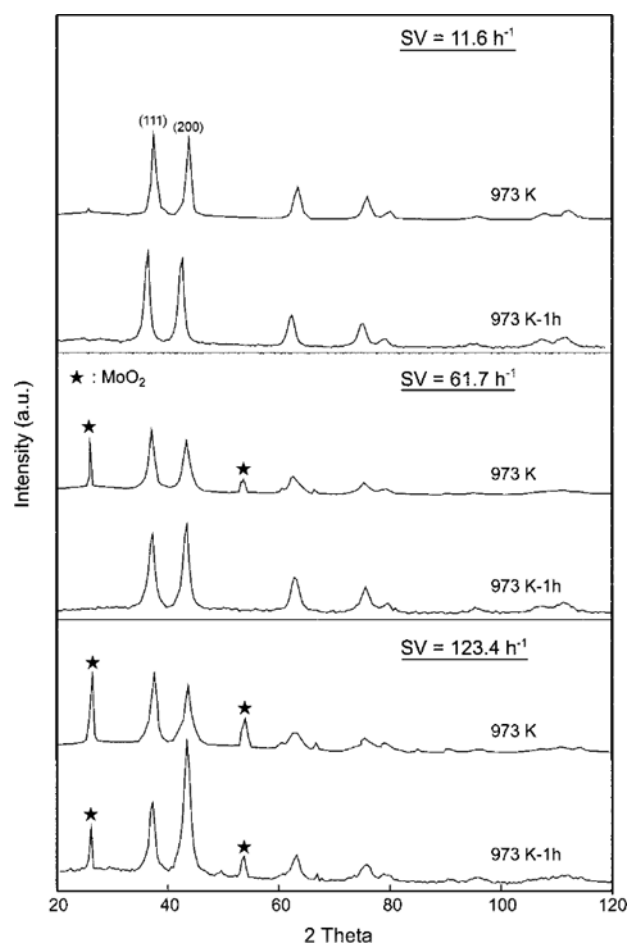

Fig. 5. Comparison of XRD patterns of Mo nitride measured at the end of temperature programming to 973 K and after being held at 973 K for another 1 hour.

ture ramping. As shown in Fig. 4, no change except intensity was observed during temperature-programmed reduction up to 673 K.

portant role in the development of the (200) plane of Mo_2N, which seems to be essential to produce high surface area Mo_2N.

2. Benzothiophene HDS and Indole HDN Reaction

Benzothiophene HDS and indole HDN reaction were performed on the prepared Mo nitride catalysts to investigate their catalytic properties. The catalytic activities of Mo nitrides for benzothiophene HDS and indole HDN were well correlated with their surface area (Fig. 6). Since indole and benzothiophene have the same chemical structure other than the heteroatom (N, S), their HDN and HDS activities can give useful information on their mechanisms. If the reactions are governed by the step of the C-N and C-S bond cleavage, the HDS activity will be higher than HDN activity, because the C-N bond is stronger than the C-S one. As expected, the activity of benzothiophene HDS was much higher than that of indole HDN
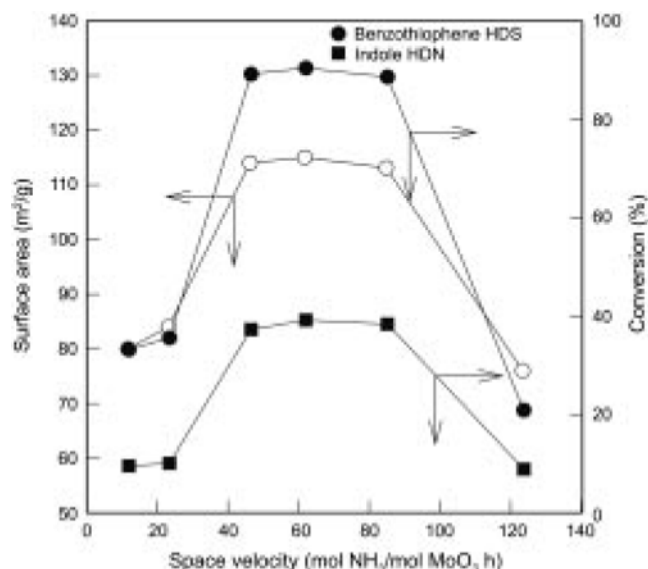

Fig. 8. Influence of reaction temperature on the product distribution of benzothiophene HDS over T4 catalyst.

Fig. 6. Correlation of reaction activities with the surface area of Mo nitride catalysts (Reaction temp. = 773 K).

Fig. 9. Influence of reaction temperature on the product distribution of benzothiophene HDS over T6 catalyst.

(Fig. 6). Therefore the step of C-S and C-N bond cleavage is believed to be the rate-determining step in the benzothiophene HDS and indole HDN reactions.

Figs. 7, 8 and 9 show plots of the variation in selectivity with temperature for the products associated with benzothiophene HDS over T1, T4 and T6 catalyst, respectively. At low reaction temperature, ethylthiophenol and ethylbenzene were the main products. On T1 and T6 catalysts, ethylthiophenol was then converted gradually to ethylbenzene, and on T4 catalyst (having the highest surface area) was observed a sharp drop of ethylthiophenol selectivity together with a rapid increase in ethylbenzene selectivity.

Figs. 10, 11 and 12 show the influence of reaction temperature on the product distribution of indole HDN over T1, T4 and T6 catalyst, respectively. Similar changes in selectivity were observed on
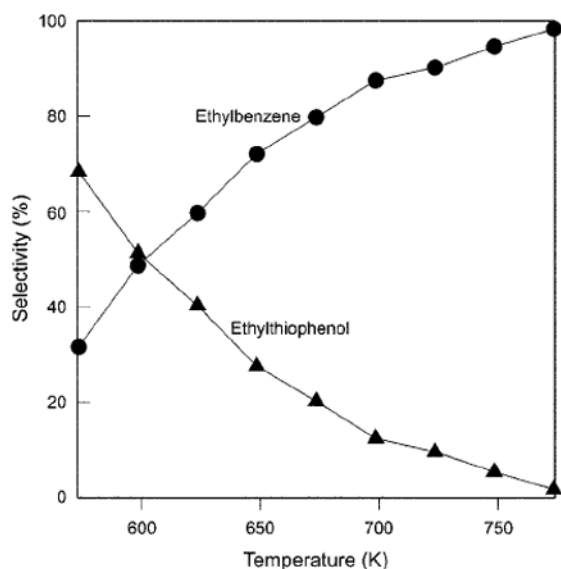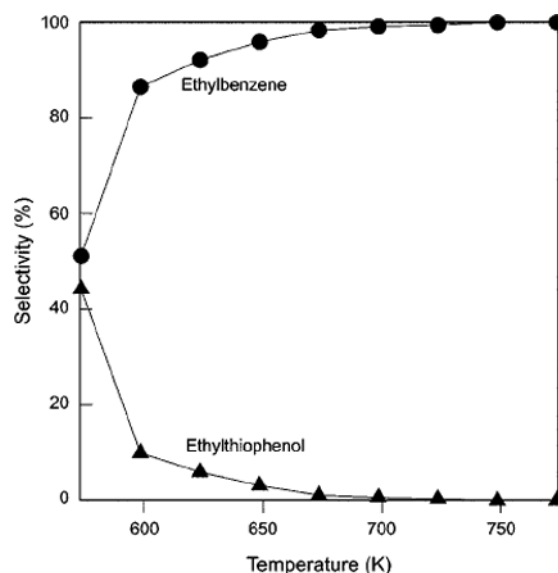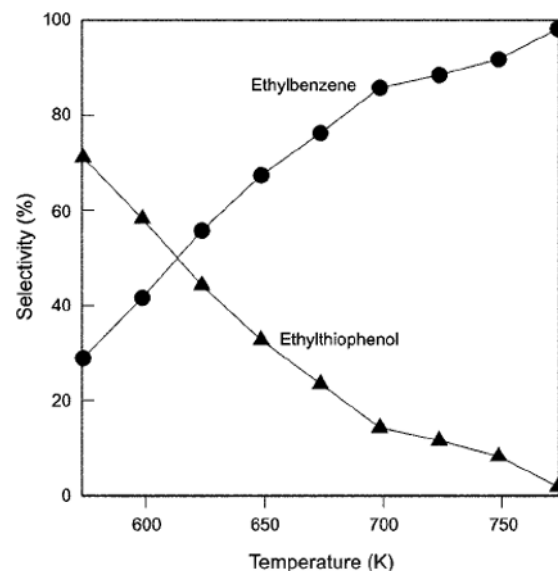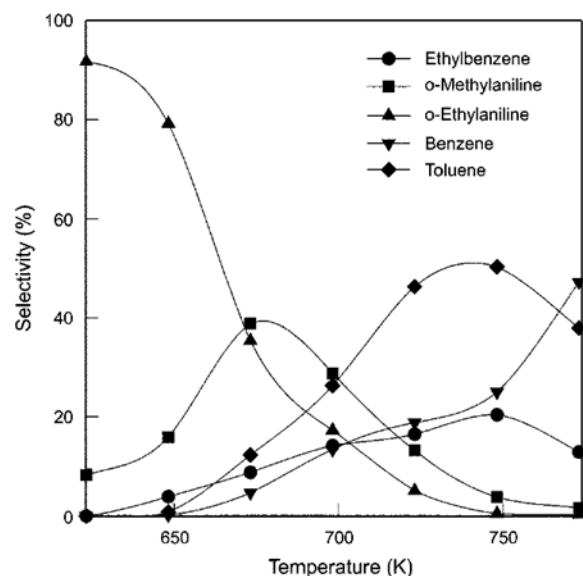

Fig. 7. Influence of reaction temperature on the product distribution of benzothiophene HDS over T1 catalyst.

Fig. 10. Influence of reaction temperature on the product distribution of indole HDN over T1 catalyst.
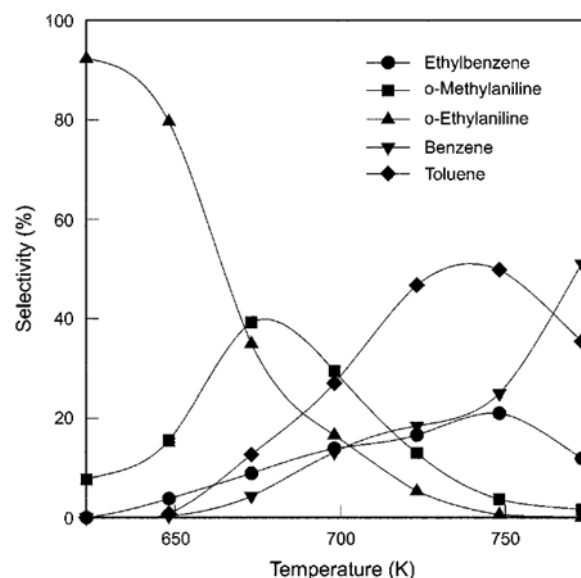

Fig. 12. Influence of reaction temperature on the product distribution of indole HDN over T6 catalyst.
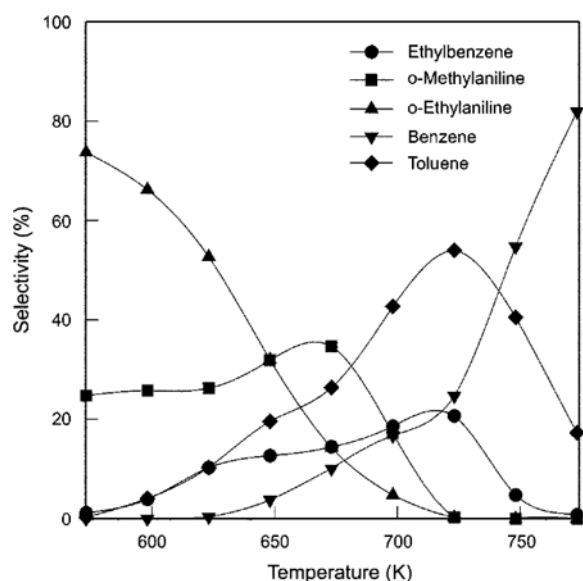

Fig. 11. Influence of reaction temperature on the product distribution of indole HDN over T4 catalyst.

Fig. 13. Proposed reaction pathways of indole HDN and benzothiophene HDS over Mo nitride catalyst.

all the catalysts. The selectivity of o-ethylaniline, the major product at low temperature, fell almost to zero by the time the temperature reached 773 K. The selectivity of o-methylaniline rose to a maximum at 673 K and then decreased monotonically, approaching zero at about 773 K. The production of ethylbenzene and toluene became more outstanding in proportion to the decreasing selectivity of o-ethylaniline and o-methylaniline, and then began to drop at a temperature between 723-748 K. Above the temperature at which the rate of ethylbenzene and toluene reached a maximum, benzene selectivity increased rapidly, probably due to the dealkylation of ethylbenzene and toluene.

Based on the above results, the reaction of benzothiophene HDS and indole HDN over Mo nitride catalysts can be proposed to pro-
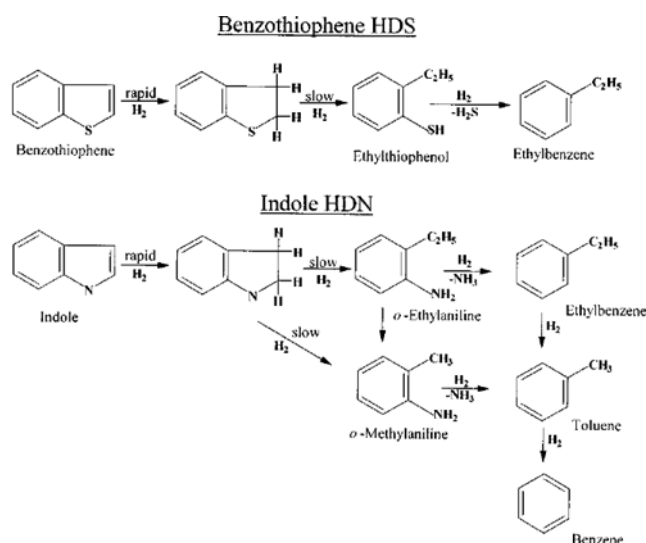
ceed through the paths shown in Fig. 13. The initial stage is thought to proceed via addition of hydrogen on the benzothiophene and indole to form tetrahydrobenzothiophene and indoline, respectively. Tetrahydro-benzothiophene and indoline undergo the cleavage of C-S and C-N bond to form ethylthiophenol, o-ethylaniline and o-methylaniline in part. Further hydrogenation of ethylthiophenol, o-ethylaniline and o-methylaniline produces ethylbenzene and toluene. In indole HDN reaction, dealkylation of ethylbenzene and toluene occurs to produce benzene.

Abe et al. [Abe et al., 1993] reported that the reaction mechanism is similar for HDS of benzothiophene and HDN of indole, and rapid hydrogenation of the heterocyclic ring is followed by hydrogenolysis of the X-C bond in the saturated ring and release of the heteroatom as H_2S and NH_3.

In both reactions no evidence for the aromatics hydrogenation

was found, and therefore Mo nitride can be an effective hydrotreating catalyst with less consumption of expensive hydrogen.

CONCLUSION

Molybdenum nitrides were prepared by temperature-programmed reduction of MoO_3 with flowing NH_3, and were used for indole HDN and benzothiophene HDS. The space velocity of NH_3 affected the surface area of Mo nitride greatly. Too low or high space velocity was inadequate to produce Mo nitride with high surface area, so there existed an optimum space velocity to have the highest surface area. The linear temperature ramping rate higher than 2.5 K/min in the β1 temperature range decreased the surface area significantly, while the surface area was hardly affected by the temperature ramping rate in the β2 temperature range.

As the reduction temperature was increased from 673 K to 723 K, MoO_3 transformed gradually into the intermediates of MoO_2 and Mo oxynitride, which were then converted to Mo_2N at 973 K. The MoO_2 intermediate showed a tendency to be converted specifically to the (200) plane of Mo_2N. So MoO_2 seemed to play an important role in producing a high surface area Mo nitride.

The catalytic activities of Mo nitrides for indole HDN and benzothiophene HDS were well correlated with their surface areas. The cleavage of C-N and C-S bond was believed to be the rate-determining step, and the reaction pathways were proposed on the basis of the selectivity changes during the temperature-programmed hydrotreating reactions. In both reactions, aromatics were not further hydrogenated, and Mo nitride could be an effective hydrotreating catalyst with less consumption of hydrogen.

ACKNOWLEDGMENT

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