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TPD and XRD studies of molybdenum nitride and its activity for hydrodenitrogenation of carbazole

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Abstract

The nitrided MoO_3 catalysts formed using two kinds of treatment with either NH_3 or He after nitriding were studied by temperature-programmed desorption and X-ray diffraction analyses. The catalysts were cooled to room temperature in either flowing NH_3 or He (NH or HE catalyst) after nitriding at 773, 973 and 1173 K with NH_3. The activities of the catalysts were determined during the hydrodenitrogenation of carbazole at 573 K and 10.1 MPa total pressure. MoO_2, γ-Mo_2N, and Mo metal were mainly formed in the NH catalysts nitrided at 773, 973 and 1173 K, respectively. Mo oxides and metals in the NH catalysts were nitrided to γ-Mo_2N and β-$Mo_2N_{0.78}$ with low crystallinity during TPD. The surface area of the NH and HE catalysts nitrided at 773 K increased to 66 and 59 $m^2\,g^{-1}$ maximum from 1.1 $m^2\,g^{-1}$ of fresh MoO_3, respectively, but decreased as the nitriding temperature increased to 973 K and 1173 K. The HE catalysts per surface area were more active than the NH catalysts for both the overall HDN reaction and hydrogenation, and the 1173 K-nitrided catalysts were highest. On the other hand, the NH catalysts were more active than the HE catalysts for C–N hydrogenolysis and the 973 K-nitrided catalyst showed a maximum activity for C–N hydrogenolysis.

Keywords: Molybdenum Nitride; HDN; Carbazole; XRD; TPD

1. Introduction

The synthesis and structure of unsupported Mo nitride have been extensively studied. The catalytic properties of the Mo nitrides are governed by their bulk composition and surface structure. Since the large surface area of the material makes it a particularly promising compound for heterogeneous catalysis, several methods for the preparation of refractory materials with large surface area have been developed; Volpe and Boudart [1] reported the synthesis of (fcc) γ-Mo_2N with a large surface area (180 $m^2\,g^{-1}$) using the temperature-programmed reaction of MoO_3 with NH_3 in a range from 630 K to 980 K. Jaggers et al. [2] also stressed the importance of the reaction intermediates in determining the surface areas and constituent phases. They found that the solid-state reaction of MoO_3 with NH_3 proceeds through two parallel reaction pathways: $MoO_3 \rightarrow MoO_xN_{1-x} \rightarrow \gamma$-$Mo_2N$ and $MoO_3 \rightarrow MoO_2 \rightarrow \gamma$-$Mo_2N + \delta$-MoN. The formation of oxynitride, MoO_xN_{1-x}, resulted in a large increase

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in surface area, which was due to the pseudomorphological nature of the reaction, while the formation of MoO_2 and Mo metal led to smaller surface area materials. Much less attention has been given for examining the change in the surface structure and composition of the catalysts such as Mo and nitrogen species after treatment of the molybdena–alumina precursor in flowing NH_3 or He gas.

Temperature-programmed desorption (TPD) is a useful technique for determining the presence of Mo and nitrogen species adsorbed on the catalyst surfaces. Gaseous products evolved from the catalysts characterize the Mo and nitrogen species of the catalysts during TPD. When TPD is used in combination with XRD measurements for unsupported or near-bulk Mo nitrides, they can provide further structural information on the Mo nitrides which coexist with the oxide, nitride and metal forms. In this work, the application of these techniques is demonstrated for the surface species and composition of the MoO_3 treated with NH_3 at 773, 973 and 1173 K, followed by cooling in NH_3 or purging with He followed by cooling in He. The effects of the treatment after nitriding of the MoO_3 on Mo and nitrogen species of the catalysts are determined. The activity and the selectivity of the catalysts are also studied for the HDN of carbazole at 573 K and 10.1 MPa total pressure.

2. Experimental

2.1. Catalyst preparation

Hydrogen and He (99.999%) were dried by passing them through Deoxo units (SUPELCO Oxysorb) and a Linde 13X molecular sieve trap prior to use. NH_3 (99.999%) was used without further purification. MoO_3 contained 97.1% MoO_3 in 2.9% γ-Al_2O_3 as a binder (Nikki Chemical). The mixed alumina and ammonium paramolybdate were molded into 3 mm o.d. pellets with a kneader. After being dried at 393 K for 24 h and then calcined at 823 K for 3 h, the pellets were crushed and sieved to 10–20 mesh (0.85–1.70 mm) granules for activity measurement, and ground for characterization of the catalysts. The MoO_3 was packed on a fritted plate in a quartz microreactor, which consisted of a 20 mm long quartz tubing of 10 mm o.d., attached at both sides with 50 mm long quartz tubing of 6 mm o.d. The MoO_3 sample was heated at 723 K in air for 1 h and cooled to 573 K, and then nitrided with pure NH_3 at 49.6 μmol s^{-1} from 723 K to 773, 973 and 1173 K at a rate of 1 K min^{-1} and held at this temperature for 3 h. After nitriding two alternative treatments were performed. In the first, the sample was cooled from the nitriding temperature to room temperature in flowing NH_3. In the second treatment, the NH_3 was switched to He gas at each of the three nitriding temperatures after nitriding. The sample was purged at 973 K in He for 1 h, and then cooled to room temperature in flowing He.

Abbreviated notations of the catalyst are used throughout this paper as shown in Table 1. For example, NH-L denoted 97.1% Mo/Al_2O_3 nitrided at 773 K in NH_3 for 3 h and followed by cooling to room temperature in flowing NH_3, while HE-H denotes 97.1 wt% Mo/Al_2O_3 nitrided at 1173 K in NH_3 for 3 h and followed by cooling to room temperature in flowing He after purged with He at 973 K for 1 h.

2.2. Analysis of surface area, nitrogen content, and molybdenum content

The specific surface area of the catalyst was measured by nitrogen adsorption using a standard volumetric BET apparatus after evacuation at 473 K and 1 Pa for 2 h. Nitrogen content was analyzed with a Perkin–Elmer CHN elemental analyzer for both the NH and He catalysts. Molybdenum analysis was done using atomic absorption spectroscopy.

2.3. Temperature-programmed desorption

TPD was performed for the nitrided catalysts under in situ conditions after preparation of the Mo nitrides. The nitrided catalyst was heated to room temperature in flowing He for 1 h after nitriding, and then heated to 1263 K at a rate of 0.167 K s^{-1} at a He flow of 11.1 mmol s^{-1}. The gases desorbed from the catalyst were monitored on-line using a quadrupole mass spectrometer (ULVAC, MSQ-150A) equipped with a variable-leak valve heated using heating tape about 350 K. The desorption rate of N_2, H_2, NH_3 and water were calculated by calibration curves for each gas.

Table 1
The surface area and the amount of N_2 desorption from the samples during TPD

Sample[a]	Surface area[b] ($m^2\ g^{-1}$)	Desorption uptake of N_2 and H_2					
		N_2 (mmol g^{-1})	NH_3 (mmol g^{-1})	Total N[c] (N_2+NH_3) (mmol g^{-1})	H_2 (mmol g^{-1})	Total H (H_2+H_2O+NH_3)	H/N
NH-L	66	0.88	0.03	0.90	0.19	0.57	0.26
HE-L	59	0.906	0.013	0.90	0.094	0.241	0.13
NH-M	33	0.54	0.05	0.565	0.09	0.40	0.71
HE-M	18	0.293	0.008	0.297	0.075	0.202	0.34
NH-H	8	1.63	0.09	1.68	0.105	0.77	0.23
HE-H	6	0.573	0.004	0.575	0.0113	0.0385	0.034

[a] The NH samples were cooled in flowing NH_3 to room temperature after nitriding a fresh MoO_3 sample (surface area, 1.1 $m^2\ g^{-1}$) to 773 K (L), 973 K (M), and 1173 K (H). The HE samples were nitrided at 773 K (L), 973 K (M), and 1173 K (H), purged in flowing He at 973 K for 1 h, and cooled in flowing He to room temperature.
[b] Evacuated at 473 K and at 1 Pa.
[c] N_2: on a basis of N_2.

2.4. X-ray diffraction

The changes in the composition of the catalysts were studied by interrupting the temperature program at the points corresponding to the labeled points (i.e., A, B, and C) in the TPD experiments. The compositions of the intermediate and final products were measured using XRD. X-ray diffraction powder analysis was performed with Ni-filtered CuK_α radiation (λ=1.5418 Å) using a Rigaku X-ray diffractometer operating at 30 kV and 20 mA with a scanning speed of $5^\circ\ min^{-1}$ from $2\theta=5^\circ$ to $2\theta=120^\circ$.

2.5. Method of activity test

The HDN of carbazole was carried out in a high pressure flow system. The microreactor was a 325 mm long stainless steel tube of 17.3 mm o.d. and 3.2 mm thickness. The HDN of carbazole on the nitrided HE and NH catalysts was conducted at 573 K and 10.1 MPa in a down-flow fixed-bed microreactor using 0.25 wt.% carbazole in xylene. Catalyst loadings were 2.0 g. Products of the reaction were quantitatively analyzed using FID gas chromatography with 1% Silicone OV-17 [3]. The rates of conversion of carbazole (overall HDN rate), the formation of the denitrogenated compounds (C–N hydrogenolysis rate), and of the hydrogenated carbazole compounds (hydrogenation rate), were calculated and reported as molecules $h^{-1}\ m^{-2}$.

3. Results and discussion

3.1. BET surface area

The surface areas of the NH and HE catalysts are shown in Table 1. The surface area of the NH catalyst increased to 66 $m^2\ g^{-1}$ from 1.1 $m^2\ g^{-1}$ after a nitriding treatment of 773 K for the fresh sample, but decreased to 33 $m^2\ g^{-1}$ as nitriding temperature increased from 773 K to 1173 K. For the HE catalysts, the surface areas showed the same trend of decreasing surface area with increasing nitriding temperature of the NH_3-cooled catalysts. The NH catalysts had a higher surface area than the HE catalysts at the same nitriding temperature. It appears that cooling of the nitrided catalysts in NH_3 makes smaller particles and better heterogeneity of the surface than that in He. For both the NH_3 and He treated catalysts, a higher nitriding treatment lowered the surface area of the catalysts, because of sintering of the catalysts at high temperature.

3.2. Changes in the composition of 773 K-nitrided catalyst during TPD

The TPD profile for the NH-L catalyst is shown in Fig. 1(a). The TPD shows one large peak of N_2 desorption at 778 K with peaks at 978 and 1034 K. The peak of N_2 desorption at the low temperature was accompanied by one peak of H_2 desorption at the

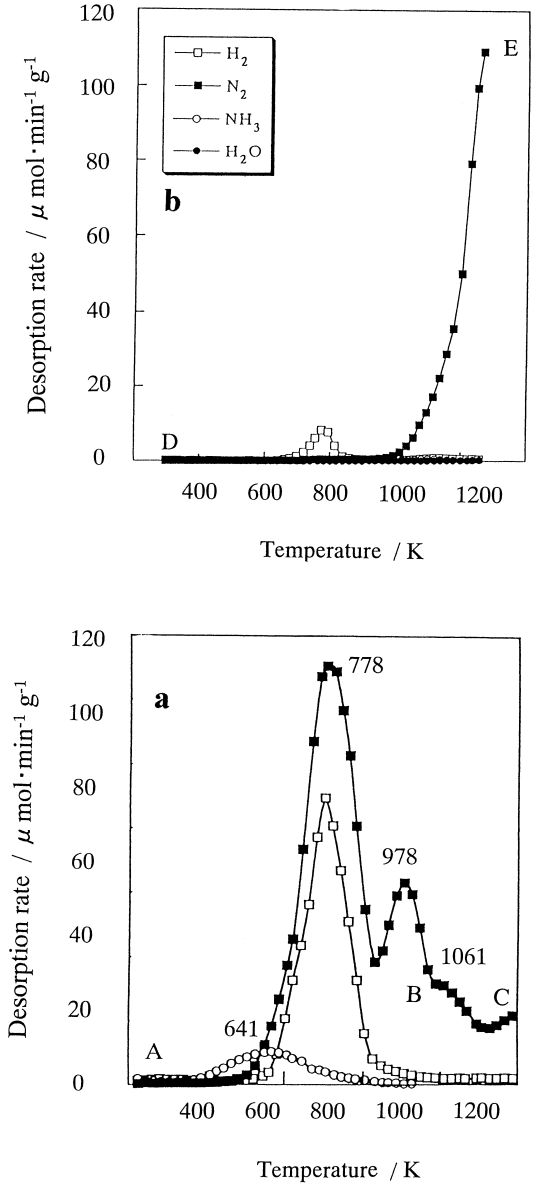

Fig. 1. Temperature-programmed desorption of the (a) NH-L and (b) HE-L catalyst. (■) N_2, (□) H_2, (○) NH_3, and (●) H_2O.

magnitude of 60% N_2 desorption. When adsorbed NH_3 was decomposed to release N_2 and H_2 from the catalyst during TPD, the molar ratio of H_2 to N_2 gave a stoichiometric value of 3.0. If MoO_3 was reduced to MoO_2 with H_2 desorbed from the catalyst, water was evolved. However, no water was formed in the TPD. From this result, the adsorbed nitrogen species contain nonstoichiometric NH_x (x<3), which reacts and rearranges on the surface to desorb N_2 and H_2. In this TPD experiment, the desorption of H_2O was significant with NH-L but scarcely observed for the other catalysts. The XRD analysis for the NH-L and HE-L showed the presence of MoO_2 in Fig. 2. H_2O ought to have been formed during TPD if Mo oxynitride was decomposed below 1000 K. The only other possibility is the formation of Mo oxynitride in the NH-L which desorbed H_2O above 1123 K during TPD.

The X-ray powder diffraction analysis was undertaken to determine the composition and crystallinity of the intermediates during TPD. For the NH-L catalyst, the as-prepared catalyst did not consist of γ-Mo_2N but MoO_2 with low intensity (1 K cps), as shown in Fig. 2(A). When the catalyst was heated to 933 K (Point B), MoO_2 was slightly altered to γ-Mo_2N (Fig. 2(B)) with low crystallinity (0.5 K cps) while desorbing N_2 gas. Further heating to 1270 K (Point C) enhanced the growth of β-$Mo_2N_{0.78}$ and γ-Mo_2N, although MoO_2 was still present as a major compound with large crystallinity (5 K cps). These results suggested that the second peak of N_2 desorption at 1034 K was due to the release of N_2 gas during the transformation of γ-Mo_2N to β-$Mo_2N_{0.78}$. NH_x adsorbed on the NH-L catalyst was expected to affect the composition and structure of the sample during TPD. From the XRD analysis, NH_x adsorbed on the catalyst nitrided MoO_2 to form γ- and β-$Mo_2N_{0.78}$ during TPD and lowered to XRD intensity of MoO_2 by forming small particles of MoO_2. NH catalysts have larger surface areas than HE catalysts, consistent with the hypothesis of small particles. We believe that Mo oxide, nitride, and metal particles on the NH catalyst became smaller when nitrogen species such as NH_x (x=0∼3) accumulated and adsorbed on the catalyst during cooling in flowing NH_3.

For the HE-L catalyst, the TPD profile (Fig. 1(b)) and XRD pattern (Fig. 2(D) and (E)) are significantly different from those for the NH-L catalyst. No large N_2 peak was observed at 818 K but the desorption of N_2 was significantly increased above 1000 K during TPD. The intensity of the XRD pattern for the HE-L catalyst was extremely high (8 K cps in Point D in Fig. 1(b)). The process, an annealing of the catalysts purged and cooled to room temperature in flowing He, resulted in good crystallinity of MoO_2. The catalyst,

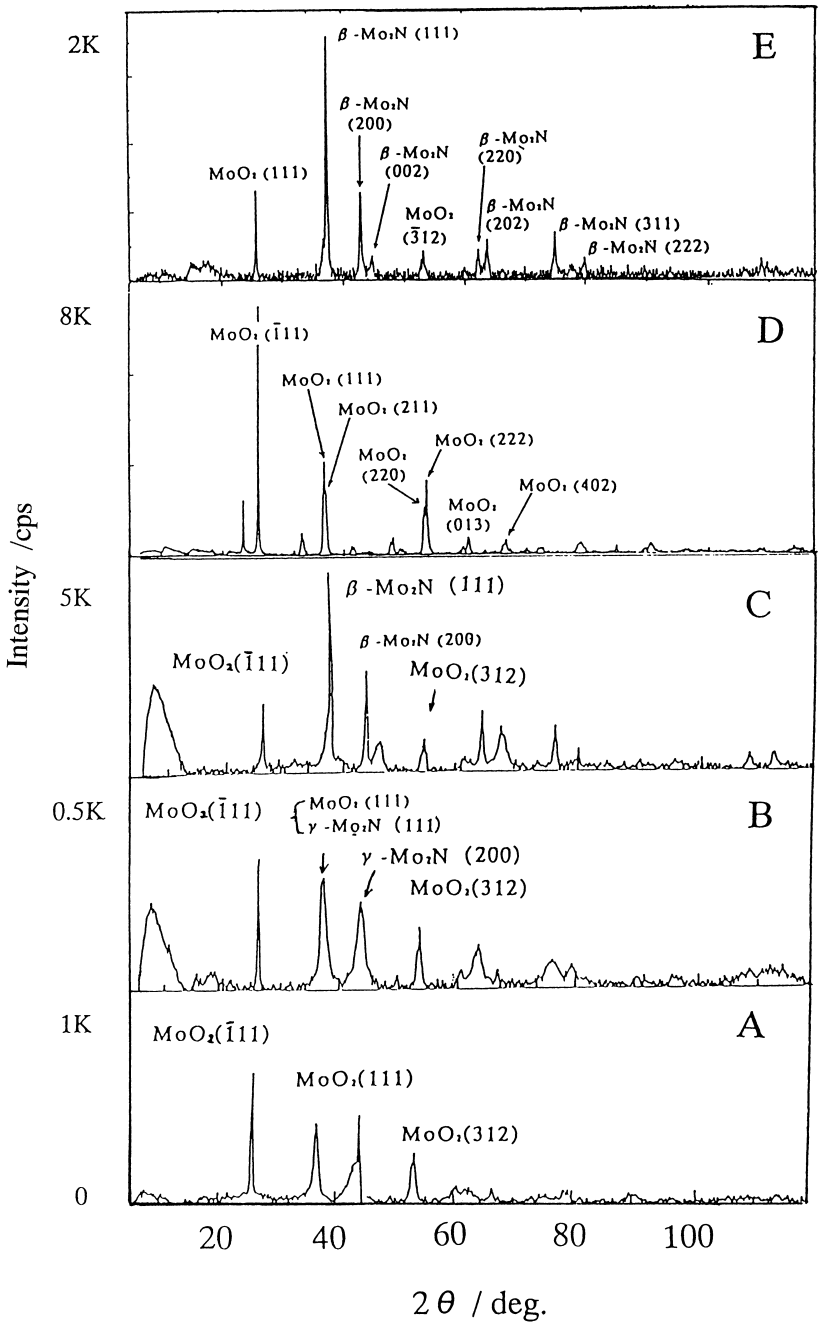

Fig. 2. XRD patterns of NH-L and HE-L catalysts. (A) As-prepared NH-L sample (point A in Fig. 1(a)), (B) the intermediate heated to 1013 K (point B in Fig. 1(a)), (C) the sample at 1270 K (point C in Fig. 1(a)), (D) as-prepared HE-L sample (Point D in Fig. 1(b)), (E) the sample at 1202 K (point E in Fig. 1(b)).

heated to 1270 K (point E in Fig. 1(b)), contained β-$Mo_2N_{0.78}$ and MoO_2 but not γ-Mo_2N as shown in Fig. 2(E). There is probably a route for the direct nitridation of MoO_2 to β-$Mo_2N_{0.78}$ with adsorbed NH_x, but no direct route from γ-Mo_2N to β-$Mo_2N_{0.78}$ for the HE-L catalyst during TPD. In contrast, for the NH-L catalyst, MoO_2 was nitrided to form β-$Mo_2N_{0.78}$ from γ-Mo_2N formed during the topotactic rearrangement of MoO_2 [2] with adsorbed NH_x and NH_3. Moreover, a small desorption peak of H_2 at 780 K without N_2 was observed for the HE-L catalyst, suggesting the consumption of all the nitrogen content of adsorbed NH_x for the nitriding of MoO_2 to β-$Mo_2N_{0.78}$. The amount of desorbed N_2 from room temperature to 1270 K was 0.88 mmol g^{-1} on the basis of N_2 as shown in Table 1. This value is consistent with nitriding 4.9% Mo atoms of the Mo/Al_2O_3 when MoO_3 was completely converted to β-$Mo_2N_{0.78}$.

3.3. Changes in the composition of 973 K-nitrided catalyst during TPD

The TPD profile for the NH-M catalyst at 973 K is shown in Fig. 3(a). The NH-M catalyst had a smaller peak of N_2 desorption than the NH-L catalyst. Two peaks of N_2 desorption were observed at 819 K and 1001 K. N_2 for the low-temperature peak was accompanied by H_2. NH_3 and H_2O were barely detectable. The peaks of N_2 and H_2 gases at 819 K were due to the decomposition and rearrangement of NH_x adsorbed in the NH-M catalyst. N_2 desorption at 1001 K was accompanied by changes in the XRD patterns. The XRD patterns of intermediates during TPD for the NH-M catalyst are depicted in Fig. 4. When the as-prepared sample, γ-Mo_2N (Fig. 4(F)), was heated to 1073 K (G) and 1159 K (H), γ-Mo_2N was transformed to β-$Mo_2N_{0.78}$ with a high crystallinity (Fig. 4(H)). Therefore, the XRD analysis for the HE-M catalyst showed that the N_2 desorption without H_2 at the broad peak of 1001 K was due to the release of N_2 during the transformation of γ-Mo_2N to β-$Mo_2N_{0.78}$.

On the other hand, the HE-M catalyst showed only one small peak of N_2 desorption at 1040 K and a gradual increase in N_2 desorption with a desorption temperature above 1040 K as shown in Fig. 3(b). The change in the composition of the HE-M catalyst at 1040 K was estimated as follows. The as-prepared HE-M catalyst was comprised of β-$Mo_2N_{0.78}$

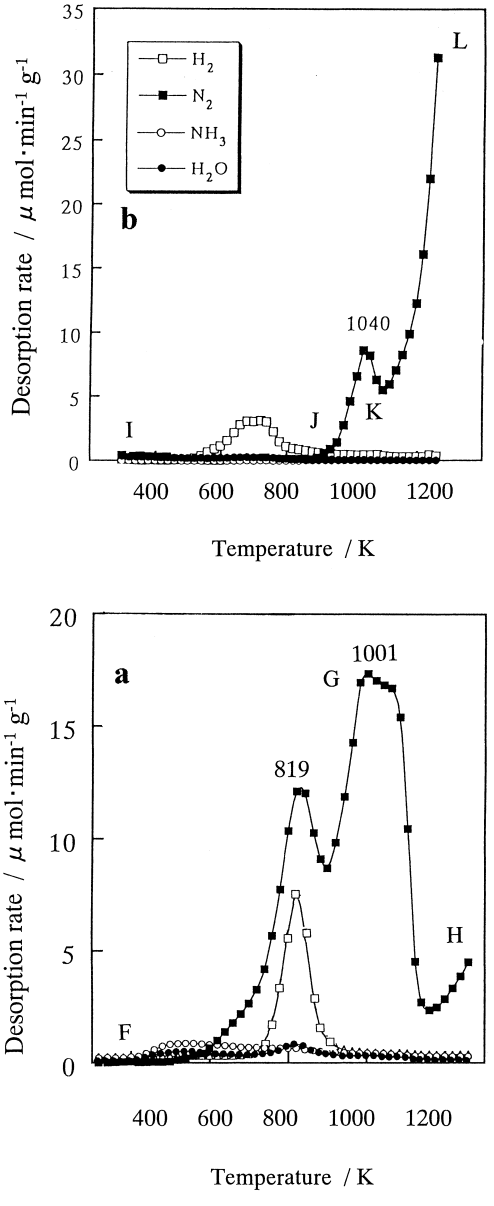

Fig. 3. TPD of the (a) NH-M and (b) HE-M catalysts. (■) N_2, (□) H_2, (○) NH_3, and (●) H_2O.

(Fig. 4(I)), indicating that γ-Mo_2N turned to β-$Mo_2N_{0.78}$ by purging in flowing He at 973 K for 1 h and subsequently cooling to room temperature. In contrast, when the sample was cooled in flowing NH_3 after nitriding at 973 K, γ-Mo_2N remained unchanged. Although β-$Mo_2N_{0.78}$ (Fig. 4(I)) was converted to γ-Mo_2N at 950 K (Fig. 4(J)) during TPD, the

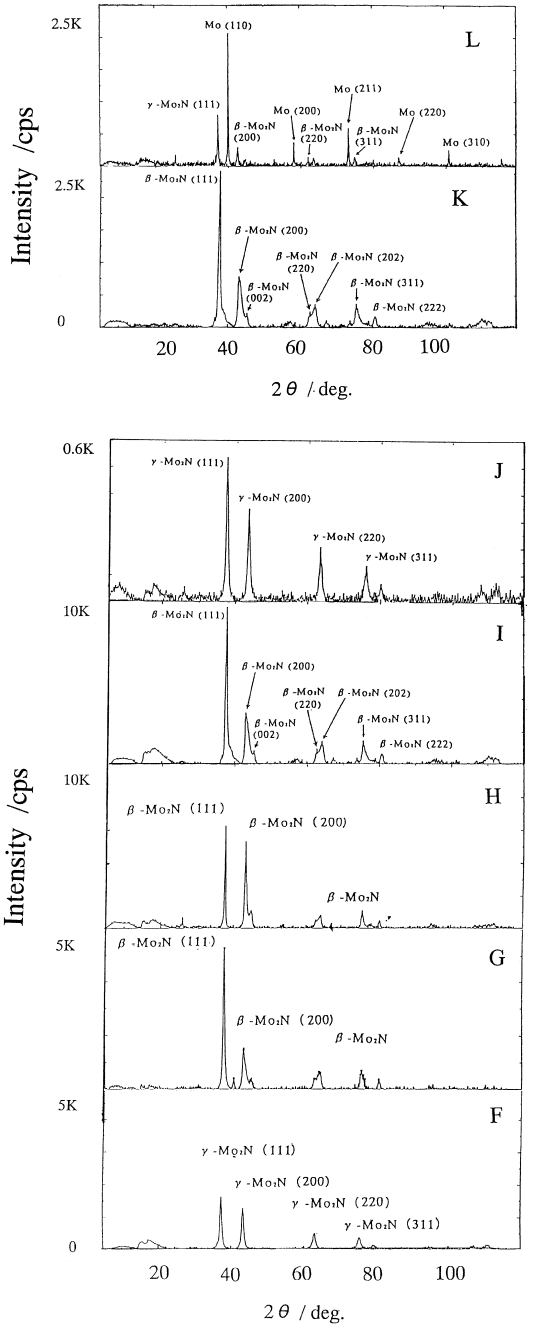

Fig. 4. XRD patterns of NH-M and HE-M catalysts. (F) As-prepared NH-M sample (point F in Fig. 3(a)), (G) the intermediate heated to 1073 K (point G in Fig. 3(a)), (H) the intermediate heated to 1159 K (point H in Fig. 3(a)), (I) as-prepared HE-M sample (Point I in Fig. 3(b)), (J) the intermediate heated to 975 K (point J in Fig. 3(b)) (K) heated to 1073 K (point K in Fig. 3(b)), (L) heated 1159 K (point L in Fig. 3(b)).

$$MoO_3 \xrightarrow{①} \gamma\text{-}Mo_2N \underset{③}{\overset{②}{\rightleftarrows}} \beta\text{-}Mo_2N_{0.78} \xrightarrow{④} Mo$$

Reaction 1: $2MoO_3 + NH_3 \rightarrow [MoO_xN_y] \rightarrow \gamma\text{-}Mo_2N + 3H_2O$

Reaction 2: $\gamma\text{-}Mo_2N \xrightarrow{1100K} \beta\text{-}Mo_2N_{0.78} + 0.11N_2$

Reaction 3: $\beta\text{-}Mo_2N_{0.78} + 0.22NHx\ (ad) \xrightarrow{950K} \gamma\text{-}Mo_2N + 0.11xH_2$

Reaction 4: $2\beta\text{-}Mo_2N_{0.78} \xrightarrow{1200K} 4Mo + 0.78N_2$

Scheme 1.

catalyst was again changed to β-$Mo_2N_{0.78}$ at 1100 K (Fig. 4(K)). This transformation of the catalyst between 900 K and 1100 K (γ-Mo_2N to β-$Mo_2N_{0.78}$) was also observed for the NH-L catalysts. Therefore, the peak in the range of 900 K and 1100 K is due to the desorption of N_2 during the transformation of γ-Mo_2N to β-$Mo_2N_{0.78}$ (Fig. 4(K)). Upon further heating to 1206 K, a part of β-$Mo_2N_{0.78}$ was altered to Mo metal(Fig. 4(L)). This result suggested that the N_2 desorption above 1100 K for the HE-M catalyst was ascribed to the liberation of N_2 gas during the reduction of β-$Mo_2N_{0.78}$ to Mo metal. Thus, adsorbed nitrogen and NH_x species make Mo nitrides and oxides unstable to form smaller particles during the heating process (Scheme 1).

3.4. *Changes in the composition of 1173 K-nitrided catalyst during TPD*

The TPD profile for the NH-H catalyst is shown in Fig. 5(a). One strong peak of N_2 desorption was observed at 1135 K with a shoulder peak at 1025 K. In the XRD data of the catalysts at that temperature, (Point M in Fig. 5(a)), the as-prepared catalyst (Fig. 6(M)) contained Mo metal (mainly Mo (110)) with a small amount of β-$Mo_2N_{0.78}$. However, when the as-prepared catalyst was heated to 773 K (Point N in Fig. 5(a)) a part of the Mo metal was altered to β-$Mo_2N_{0.78}$ that grew with very low crystallinity (Fig. 6(N)). Upon further heating to 1273 K (Point O), β-$Mo_2N_{0.78}$ completely changed to Mo metal again with the recovery of about 70% of its crystallinity after the desorption of N_2 during TPD. This result supported the reduction of β-$Mo_2N_{0.78}$ to Mo metal at ca. 1135 K. Adsorbed NH_x appears to make Mo_2N susceptible to reduction. The peak of N_2 desorption at 1025 k for NH-H corresponded with that at

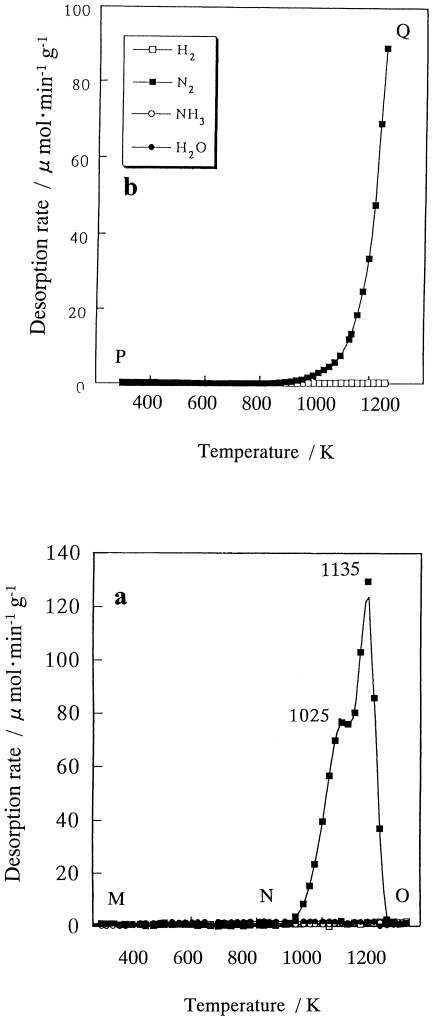

Fig. 5. TPD of the (a) NH-H and (b) HE-H catalysts. (■) N_2, (□) H_2, (○) NH_3, and (●) H_2O.

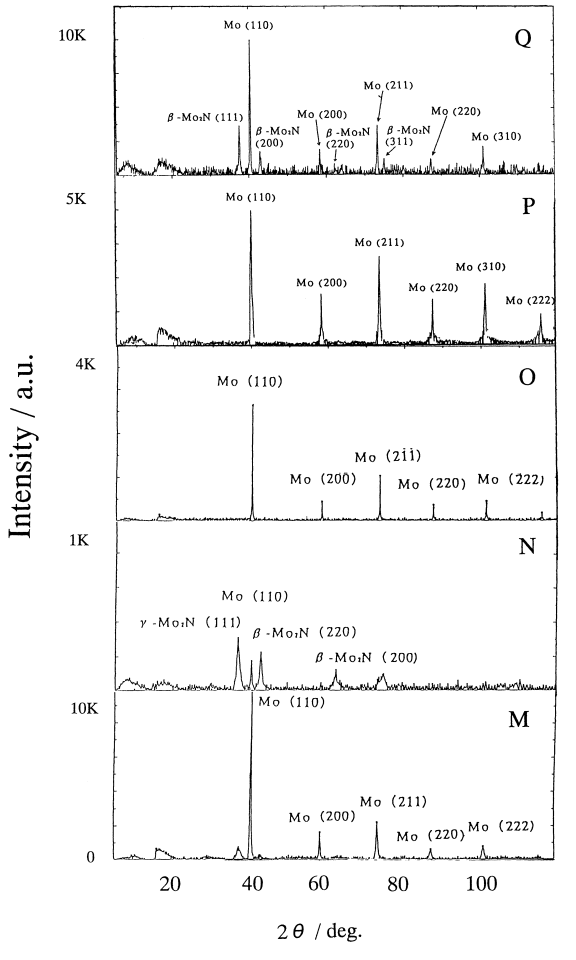

Fig. 6. XRD patterns of the NH-H and HE-H catalysts. (M) As-prepared NH-H (point M in Fig. 5(a)), (N) intermediate at 773 K (point N in Fig. 5(a)), (O) at 1200 K (point O in Fig. 5(a)), (P) as-prepared HE-H sample (Point P in Fig. 5(b)), (Q) at 1257 K (point Q in Fig. 5(b)).

1034 K for the NH-L and those at 1001 K for the NH-M and HE-M catalysts. Therefore, the major peak of N_2 desorption at 1135 K and the shoulder peak at 1025 K were due to the release of N_2 during the reduction of β-$Mo_2N_{0.78}$ to Mo metal and the transformation of γ-Mo_2N to β-$Mo_2N_{0.78}$, respectively. The amount of N_2 desorbed on heating NH-H to 1159 K during TPD corresponded to 9% of MoO_3 in the Mo/Al_2O_3 being converted to β-$Mo_2N_{0.78}$. Furthermore, neither H_2 nor H_2O were desorbed from the catalyst between 300 K and 1270 K. This result indicates that nitrogen but not NH_x (x=1∼3) or hydrogen were present in NH-H. Han and Schmidt [4] reported that no H_2 above 600 K in flash desorption spectra on Mo (100). Bafrali and Bell [5] also found no H_2 desorbed from Mo metal (100) above 600 K during TPD, though H_2 was evolved at 177, 227 and 300 K.

On the other hand, for the HE-H catalyst (Point P in Fig. 5(b)), the desorption of N_2 was not observed below 850 K but sharply increased above 850 K. The as-prepared catalyst (P in Fig. 5(b)) was composed of Mo metal with low crystallinity (Fig. 6(P)). When the as-prepared catalyst reached 1257 K, XRD revealed highly crystalline Mo metal together with a

small amount of β-$Mo_2N_{0.78}$ (Fig. 6(Q)). Table 1 shows that H_2 was produced from the HE-L and HE-M catalysts but not from the HE-H catalyst, indicating that NH_x was present on the Mo oxides and nitrides. However, NH_x was not adsorbed on Mo metal but nitrogen was. Adsorbed nitrogen species nitride Mo oxides and Mo metals to form small particles. Oyama and Boudart [6] also reported that molybdenum powder takes up nitrogen after ammonia synthesis corresponding to 4 or 5 layers of Mo_2N. Adsorbed atomic nitrogen is reported to be desorbed from polycrystalline molybdenum [7,8] at about 1210 K [9]. The strength of N adsorption is confirmed by the fact that N_2 desorbs from nitrided Mo(100) at only above 1200 K. Maning and Schmidt also reported that N_2 on Mo(110) desorbs from a single binding state at a peak temperature of 1460 K [10]. Matsushita and Hansen [7] reported that nitrogen is adsorbed by clean Mo metal (110) in two well-defined states: one stable up to 1273 K, and the other one stable only below 130 K. Furthermore, on Mo(100), there are two peaks, one at 1350 K [5], the other at 193 K. In conclusion, the He-cooled catalysts are annealed highly crystalline products from which NH_x has been purged during the change from γ-Mo_2N to β-$Mo_2N_{0.78}$, whereas the NH catalysts remain polycrystalline in the presence of NH_3 gas and adsorbed NH_x. The XRD data on NH catalysts indicates Mo oxides remained on the as-prepared NH-L catalyst but Mo nitrides were formed in the NH-M catalyst. Desorption at 820–845 K of N_2 and H_2 are due to adsorbed NH_x. In the NH-L catalysts, the second peak in the TPD arises from the evolution of N_2 during the transformation of γ-Mo_2N to β-$Mo_2N_{0.78}$.

3.5. Catalyst test

The major denitrogenated product was bicyclohexyl together with small amount of cyclohexylhexene and hexylcyclohexane. The primary hydrogenated product was tetrahydrocarbazole, but traces of other hydrogenated carbazole compounds such as hexahydrocarbazole, octahydrocarbazole, and perhydrocarbazole were observed. The rates for the C–N hydrogenolysis and hydrogenation in the HDN of carbazole are given in Figs. 7 and 8, respectively. The results are also given in Table 2. The rate of the hydrogenation for the HE catalysts increased with

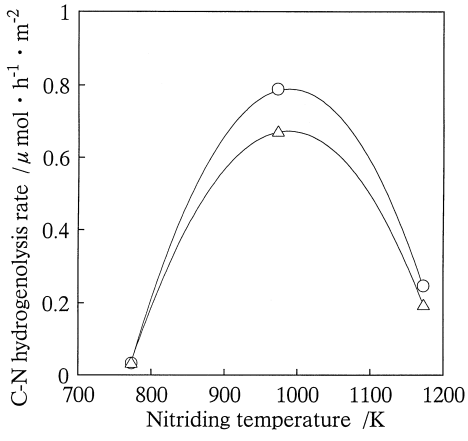

Fig. 7. The C–N hydrogenolysis rates of the (○) NH and (△) HE catalysts for the HDN of carbazole at 573 K and 10.1 MPa total pressure.

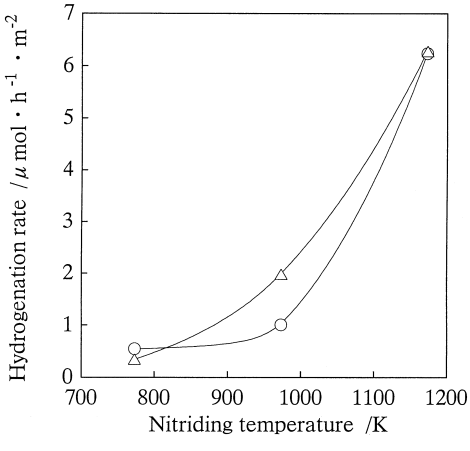

Fig. 8. The hydrogenation rates of the (○) NH and (△) HE catalysts for the HDN of carbazole at 573 K and 10.1 MPa total pressure.

increasing nitriding temperature and exhibited a greater rate than those for the NH catalysts. The HE-H was the most active in the hydrogenation of carbazole. For the C–N hydrogenolysis, the activity of the NH catalyst was greater than that of the HE, and the NH-M was the most active.

3.6. Mo species and HDN activity

The NH-M catalyst was the most active for C–N hydrogenolysis of carbazole and the HE-M catalyst exhibited the second highest activity. The NH-M

Table 2
HDN of carbazole at 573 K and 10.1 MPa

Catalyst nitriding temperature	Overall[a]			C–N hydrogenolysis[b]			Hydrogenation[c]		
	(μ mol h^{-1} m^{-2})		NH/He	(μ mol h^{-1} m^{-2})		NH/He	(μ mol h^{-1} m^{-2})		NH/He
	NH[d]	HE[e]		NH	HE		NH	HE	
773 K	0.389	0.489	0.796	0.0326	0.0356	0.916	0.547	0.348	0.152
973 K	1.76	2.63	0.669	0.789	0.674	1.17	1.00	1.98	0.505
1173 K	3.94	4.36	0.904	0.248	0.197	1.26	6.24	6.28	0.993

[a] Overall HDN rate; based on the conversion of carbazole.
[b] Based on the formation of the denitrogenated compounds.
[c] Based on the conversion of carbazole.
[d] The sample was cooled in flowing NH_3 to room temperature after nitriding.
[e] The sample was cooled in flowing He to room temperature, after the sample was purged with He at 973 K for 1 h.

catalyst consisted of γ-Mo_2N but the HE-M contained γ-$Mo_2N_{0.78}$. Purging the samples with He converted γ-Mo_2N to β-$Mo_2N_{0.78}$ in HE-M. The compositions of NH-M and HE-M did not change significantly at 573 K. XRD analysis indicated the transformation of β-$Mo_2N_{0.78}$ in NH-M at 1001 K (Fig. 3(a)) and that of γ-Mo_2N in HE-M at 800 K (Fig. 3b). Moreover, the HE-H catalyst was the most active for the hydrogenation. Lower amount of reduced Mo are created on the 973 K-nitrided catalyst than on the 1173 K-nitrided catalyst. Since the HE-H was comprised of Mo metal with a small amount of β-$Mo_2N_{0.78}$, the HE-H catalyst had patches of Mo metal species formed by NH_3 treatment at 1173 K. From the results, γ-Mo_2N was most active in the C–N hydrogenolysis, β-$Mo_2N_{0.78}$ less so, and MoO_2 least. Mo metal in HE-H was highly active for hydrogenation. MoO_2 in the NH-L was not as active as Mo metals and Mo nitrides for the C–N hydrogenolysis and hydrogenation during the HDN of carbazole. Furthermore, the amorphous MoO_2 in NH-L may make it more active than the HE-L for the hydrogenation of carbazole as shown in Fig. 8.

3.7. Nitrogen amount and nitrogen species

The NH catalyst, which was cooled to room temperature in flowing NH_3 after nitriding, held much more nitrogen, as shown in Table 1. The total amount of N_2 desorbed on heating the NH-L catalyst to 1159 K was 0.90 mmol g^{-1}. Hillis et al. [11] reported that molybdenum dioxide adsorbed 1.89 mmol N_2/g-MoO_2 for 10 h at 773 K. NH-L, comprised mainly of MoO_2, desorbed half of this amount. The NH-H catalyst, consisting of Mo metal desorbed 1.68 mmol N_2/g-MoO_2 while NH-M consisting of γ-Mo_2N desorbed 0.565 mmol N_2/g-MoO_2. Aika and Ozaki [12] reported that 1.92 mmol g/Mo of N_2 was adsorbed on a reduced molybdenum metal after 69 h of nitriding in N_2 at 775 K. Bell et al. [13,14] also reported that the uptake of NH_3 on γ-Mo_2N with a large surface area (140–155 m^2 g^{-1}) at 295 K is 0.77 m mol g^{-1}. Our result of the amount of adsorbed nitrogen was less than those in the literature by a factor of 0.7–0.9 because of the 3 h nitriding time.

The N_2 desorption was thought to proceed through the recombination of adsorbed nitrogen on the surface [9]. Above 573 K, adsorbed NH_3 underwent sequential dehydrogenation to produce NH_2 and NH groups as well as N and H atoms [15,16]. The adsorption of strongly-bound H atoms, in small islands, could limit the availability of hydrogen in surface reactions [15]. Hydrogen was formed during the decomposition of NH_3 during cooling in flowing NH_3. The NH catalysts contained more NH_x (x<1.5) on the surface of the NH catalyst, but the HE catalysts contained less hydrogen in NH_x as shown in Figs. 1, 3 and 5. In the present study, nitrogen is present as an adsorbed NH_2 group and N atoms on the surface of γ-Mo_2N and alumina for the Mo/Al_2O_3 catalyst nitrided at 973 K. Furthermore, NH_3 was decomposed on both Mo(100) and nitrided Mo(100) [5], while the two steps NH_3 (s)→NH_2 (s)→NH (s) are reversible, the third (NH (s)→ N (s) + H (s)) is irreversible, reflecting the strong bonding of N_s. Thus, N_2 was desorbed from the decomposition and reconstruction of NH_x on the nitrided catalysts below 1150 K.

4. Conclusions

1. TPD experiments indicated that NH_x species are present on the surface of the nitrided catalysts and react with MoO_2 and Mo metal to form γ-Mo_2N and β-$Mo_2N_{0.78}$, respectively, during the TPD run.
2. The XRD measurement showed that molybdenum nitride is formed as γ-Mo_2N in the NH-M catalyst. For the catalysts nitrided at 773 K, there was no formation of molybdenum nitride on the surface.
3. The NH-L, -M and -H catalysts show three peaks for N_2 desorption. A large first peak of N_2 desorption at about 820 K was ascribed to the formation of N_2 accompanied with H_2, during the combination and reaction of adsorbed NH and N species on the Mo surface. The second shoulder peak of N_2 desorption at 1025–1054 K was due to the desorption of N_2 from adsorbed nitrogen on γ-Mo_2N or MoO_2 in the NH_3-cooled sample. The third N_2 peak at 1135 K was due to the evolution of N_2 during the transformation of γ-Mo_2N to β-$Mo_2N_{0.78}$.
4. Mo species was active in the C–N hydrogenolysis as follows:

$$\gamma - Mo_2N > \beta - Mo_2N_{0.78} \gg \text{Mo metal} > MoO_2$$

5. Mo species was active in the hydrogenation as follows:

$$\text{Mo metal} \gg \beta - Mo_2N_{0.78} > \gamma - Mo_2N > MoO_2$$

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