# Catalytic Activity and Surface Properties of Nitrided Molybdena–Alumina for Carbazole Hydrodenitrogenation

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The catalytic activity and surface properties of nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were studied using temperature-programmed reduction and diffuse reflectance FTIR and XPS spectroscopy. The activity of the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts was tested for the hydrodenitrogenation of carbazole. The catalytic activity of the 43.0, 58.0, 77.3, and 97.1% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts was also determined for comparison. The MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> precursors with various molybdenum loadings were nitrided by the temperature-programmed reaction with ammonia. The temperature-programmed reduction showed that the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts had a broad peak which was deconvoluted to six nitrogen peaks: four peaks due to nitrogen species adsorbed on the surface molybdenum species (MoO<sub>2</sub>,  $\gamma$ -Mo<sub>2</sub>N, and Mo metal) and alumina and two peaks due to nitrogen release from the bulk molybdenum nitride. The infrared spectra of ammonia showed that the 1173 K nitrided catalyst was less acidic than the 773 K nitrided catalyst but that its Lewis to Brønsted acidity ratio was 25 times higher. The 1173 K nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalyst had the highest TOF for the hydrodenitrogenation of carbazole. The XPS measurement showed that metallic Mo and Mo<sup>2+</sup> were predominant in the 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts and led to the hydrogenation in the hydrodenitrogenation of carbazole. © 2000 Academic Press

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## INTRODUCTION

Molybdenum oxides, nitrided with ammonia supported on a high surface area alumina, recently exhibited high activity for hydrodenitrogenation (HDN) of nitrogen compounds (1–6). These catalysts are reported to have better

selectivity for C-N bond cleavage than hydrogenation and to have HDN activity similar to or higher than that of commercial sulfided Ni-Mo catalysts on the basis of a CO or O<sub>2</sub>. There are a few studies on the surface properties and reactivity of unsupported molybdenum nitrides (7-20). Boudart et al. (7) studied nitrogen adsorption on molybdenum metal polycrystalline and reported that the surface was predominantly covered with adsorbed nitrogen and some dissociated species (N, NH, and NH<sub>2</sub>). Haddix et al. (10) studied the dynamics of ammonia adsorbed on unsupported  $\gamma$ -Mo<sub>2</sub>N using a proton NMR technique. The NMR measurement indicated that adsorbed ammonia was dehydrogenated to produce NH<sub>2</sub> and NH groups as well as N and H atoms above 573 K. Moreover, Thompson and co-workers (13) found that the reaction rate during pyridine HDN increased linearly with the amount of NH<sub>3</sub> chemisorbed in the NH<sub>3</sub>-TPD experiment, suggesting that HDN and pyridine adsorption occurred on sites that adsorbed NH<sub>3</sub>. The relationship between the surface molybdenum and the adsorbed nitrogen species and the catalytic activity of the nitrided alumina-supported catalysts during the HDN of carbazole have, however, received less attention. There are very few reports on the molybdenum oxidation state of active molybdenum species of the nitrided catalysts. Furthermore, it is not fully understood whether or not molybdenum nitride is formed on the surface of the nitrided molybdenaalumina.

For characterization, temperature-programmed reduction (TPR) with hydrogen can be used to determine the reactivity of individual molybdenum species of nitrided molybdena-alumina during the reaction of adsorbed nitrogen species associated with molybdenum species with hydrogen to release nitrogen and ammonia gases (2, 16, 19, 21). The desorption of these gases during TPR can identify the molybdenum species associated with surface and structural molybdenum compounds of the nitrided catalysts. The surface composition and molybdenum oxidation state of the Mo/Al<sub>2</sub>O<sub>3</sub> catalysts nitrided at several temperatures are determined by XPS spectroscopy. Therefore, in this study, the surface molybdenum species were determined



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according to the desorption of nitrogen and ammonia gases during TPR. A positive relationship between the molybdenum oxidation state of the nitrided catalysts and the catalytic activity for carbazole HDN was determined by XPS analysis. Furthermore, diffuse reflectance FTIR spectroscopy can determine the nature of the acid sites on the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. The relationship between the highly active molybdenum species and the activity of the catalysts for carbazole HDN is also discussed.

## **EXPERIMENTAL**

## Catalyst Preparation and Nitriding

Hydrogen and helium (99.9999%) were dried by passing them through a Deoxo unit (SUPELCO, Oxysorb) and a Linde 13X molecular sieve trap prior to use. Ammonia (Tomo-e, 99.99%), 1.0% O<sub>2</sub> in helium, carbazole (Tokyo Kasei, 99.9%), and xylene (mixed o-, m-, and p-xylene, extra pure; specific gravity 0.86) were used without further purification. MoO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with various loadings (12.5, 43.0, 58.0, 77.3, and 97.1% MoO<sub>3</sub>; Nikki Chemical Co.) were prepared as follows: Ammonium heptamolybdate was dissolved in an aqueous ammonium solution at 308 K.  $\gamma$ -Alumina xerogel was added to the ammonium paramolybdate solution, and the solution was boiled while being stirred. The solid product was dried at 473 K for 24 h and ground to a powder. For the 97.1% MoO<sub>3</sub> catalyst, ammonium paramolybdate was mechanically mixed with 2.9 wt%  $\gamma$ -alumina hydrogel as a binder. The solid product was molded into 3-mm o.d. pellets with a kneader. After drying at 393 K for 24 h followed by calcination at 823 K for 3 h in air, the pellets of the molybdena-alumina were crushed and sieved to 10 to 20 mesh (0.85 to 1.70 mm) granules for measurement of activity and to powder (above 100 mesh) for characterization. The MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was supported on a fretted ceramic disk in a tubular quartz microreactor in the catalyst pretreatment unit. The microreactor was heated externally by an oven connected to a variable temperature programmer with a chromel-alumel thermocouple positioned outside the reactor near the catalyst bed to monitor the temperature and to relay it to the PID temperature programmer. A separate thermocouple was placed at the center of the catalyst bed to measure the temperature of the catalyst. The catalyst was oxidized at 723 K for 24 h in air and cooled to 573 K in a stream of dry air, followed by a stream of pure ammonia. The temperature of the molybdena-alumina was raised from 573 to 773 (low temperature nitriding; LTN), 973 (MTN), and 1173 K (HTN) at a rate of 0.0167 K  $s^{-1}$  in a stream of ammonia at 49.6  $\mu$ mol s<sup>-1</sup> and held at the nitriding temperature for 3 h in ammonia. After the ammonia treatment, the catalyst was cooled to room temperature in a stream of ammonia for the TPR, XPS, and activity measurements. For the

FTIR measurement, the nitrided catalyst was purged with helium at 973 K for 1 h and cooled to room temperature in a stream of helium in order to prevent interference by excess ammonia. To determine the activity of the 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, the helium-cooled catalysts were also used for comparison of the ammonia-cooled catalyst. The nitrided catalysts were passivated in 1.0% O<sub>2</sub> in helium at room temperature for more than 12 h. The TPR experiment was carried out *in situ*, in order to desorb the water during TPR that interferes with the nitrogen and ammonia spectra. The space velocity of ammonia was 5096  $h^{-1}$  for the ammonia flow rate of 49.6  $\mu$ mol s<sup>-1</sup>. The following terms denote the catalysts: 12MTN denotes 12.5% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> nitrided in a stream of ammonia at 973 K for 3 h. 43HTN denotes 43.0% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> nitrided in a stream of ammonia at 1173 K for 3 h.

# Characterization

The surface area of the catalysts was measured at 78 K by nitrogen adsorption using a BET apparatus (Coulter Co., Omnisorp 100CX) after evacuation at 473 K and 1 Pa for 2 h. The nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were characterized in situ after the ammonia treatment by means of TPR. The microreactor in the TPR apparatus was constructed from a quartz tube (12 mm o.d.) with a total volume of 2.4 ml. The catalyst was held in place with a fretted ceramic disk. The temperature of the catalyst (0.2 g) was increased from room temperature to 373 K in a stream of helium and was maintained at 373 K for 1 h. after which it was heated to 1263 K at a rate of 0.167 K  $s^{-1}$  in a hydrogen flow of 11.2  $\mu$ mol  $s^{-1}$ . The desorption gases that escaped from the catalysts during TPR were monitored on-line using a quadrupole mass spectrometer (ULVAC, MSQ-150A). The spectra of the desorbed gases were obtained by curve-fitting (Microcal Co., ORIGIN) the data that were transferred from the quadrupole mass spectrometer. The surface composition of the molybdenum atoms in the nitrided catalysts was measured using a Shimadzu ESCA 3200 spectrometer with monochromatic MgK $\alpha$  exciting radiation (8 kV, 30 mA) at a pressure of  $5 \times 10^{-4}$  Pa. Argon etching was done for 5 min before the spectra were measured by XPS. The binding energy of the catalysts was referenced to Al 2p at  $74.7 \pm 0.2$  eV. Curvefitting of the Mo 3d peaks was accomplished by using linked doublets of the same full width at half-maximum (fwhm), an intensity ratio of 2/3, and a splitting of 3.2 eV for the Mo  $3d_{3/2}$ and  $3d_{5/2}$  lines (22–24). The Mo 3d spectra were fitted into five sets of Mo doublets (Mo  $3d_{3/2}$  and  $3d_{5/2}$ ) corresponding to five molybdenum species ( $Mo^{6+}$ ,  $Mo^{5+}$ ,  $Mo^{4+}$ ,  $Mo^{2+}$ , and Mo<sup>0</sup>). The acidity of the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was analyzed according to an FTIR measurement with ammonia as the probe. The catalyst was packed into an FTIR cell (Harrick Co., HVC-5). To remove the oxygen that was

adsorbed by the water that formed on the catalyst, the catalyst was reduced in a stream of hydrogen (11.2  $\mu$ mol s<sup>-1</sup>) at 773 K for 1 h, purged at 773 K with helium (11.2  $\mu$ mol s<sup>-1</sup>) for 1 h, and then cooled to room temperature in a stream of helium. Diffuse reflectance FTIR spectra of the ammonia adsorbed by the catalysts were recorded by an FTIR instrument (Nicolet, Model 740, MCT detector), equipped with a Harrick diffuse reflectance accessory. The infrared spectra were measured with a resolution of 4  $cm^{-1}$  in 100 scans at room temperature. After treatment in flowing helium at 373 K for 1 h, the catalyst was treated in a stream of 5.06% NH<sub>3</sub>/He (11.2  $\mu$ mol s<sup>-1</sup>) at 373 K for 1 h, purged with helium (11.2  $\mu$ mol s<sup>-1</sup>) for 1.5 h, and heated at elevated temperature in a stream of helium. To compare the IR spectra of the catalysts with the spectrum of the reduced catalyst, the fresh 12.5% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was reduced at 623 K in a stream of hydrogen for 3 h. The amount of CO chemisorbed on the surface of the catalysts was determined by a volumetric analyzer after evacuation (Coulter Co., Omnisorp 100CX). Before measuring the CO uptake, the catalyst (0.2 g) was pretreated in a stream of helium at 723 K for 2 h and reduced in hydrogen at 653 K for 2 h. After the reduction, the catalyst was degassed at  $10^{-2}$  Pa and at 653 K for 1 h and then cooled slowly to room temperature in a vacuum. The amount of irreversible CO uptake was obtained from the difference between the two CO isotherms which were extrapolated to zero pressure. The molybdenum content was analyzed by means of atomic absorption spectroscopy.

# Measurement of Activity

The HDN of carbazole was measured using a fixed-bed microreactor in a high-pressure flow system as described elsewhere (25). The microreactor, consisted of a stainlesssteel tube (325 mm long, 17.3 mm wide, 3.2 mm thick), the top of which was connected to a hydrogen gas cylinder and a high-pressure feeder pump and the bottom of which was connected to a high-pressure separator. Catalyst loading was 2.0 g. The passivated catalysts were reduced in the reactor at 773 K with hydrogen for 1 h at 10.1 MPa to remove water. The liquid feed, consisting of 0.25 wt% carbazole in xylene, was introduced into the reactor at 20 ml  $h^{-1}$  with a hydrogen flow of 74.4  $\mu$ mol s<sup>-1</sup> at 573 K and a total pressure of 10.1 MPa. The liquid reaction products were separated from gaseous products, such as hydrogen and ammonia, with a boiling point lower than that of the xylene solvent in the high-pressure separator. The reaction products were analyzed quantitatively by means of an FID gas chromatograph with 2% silicon OV-17 (25). The rate of carbazole HDN was calculated according to the conversion of carbazole at 573 K. The TOF  $(h^{-1})$  is given by

TOF 
$$(h^{-1})$$
 = HDN rate at 0.5 h (µmol h<sup>-1</sup> g<sup>-1</sup>)/  
irreversibly adsorbed CO (µmol g<sup>-1</sup>).

## **RESULTS AND DISCUSSION**

# Nitrogen Desorption during TPR

The desorption of nitrogen for the catalysts nitrided at 773 K during TPR (e.g., 0LTN, 12LTN, and 97LTN) is shown in Fig. 1. The profile showed only one large desorption peak of nitrogen at temperatures of 877 (97LTN), 898 (12LTN), and 900 K (0LTN); 97LTN had an additional large desorption peak above 1253 K. A small peak of ammonia was also observed around 700 K. Since the molybdenum oxide kept  $NH_x$  (x = 0-3) adsorbed on the unsupported Mo<sub>2</sub>N during cooling from the nitriding temperature to room temperature (2, 7, 18, 19), molybdenum oxides reacted with some of the adsorbed NH<sub>x</sub> during TPR to form molybdenum nitrides, and the other adsorbed  $NH_x$ species desorbed as nitrogen and ammonia gases at a desorption temperature around 877 to 900 K. Thus, treating molvbdena-alumina with ammonia at 773 K did not lead directly to the formation of molybdenum nitrides but rather to molybdenum oxides which were nitrided with adsorbed NH<sub>x</sub> at temperatures of 877 to 900 K. For the catalysts nitrided at 973 K (Fig. 2), the TPR profile for 97MTN shows three distinct peaks of nitrogen desorption at 897, 1097, and 1197 K. For 43MTN, two peaks of nitrogen desorption were observed at low and moderate temperatures but with a broad peak at 1197 K. These peaks decreased further for 12MTN. In a previous paper (4), the TPD study showed that the desorption of nitrogen was not accompanied by hydrogen above 1000 K, and therefore, the nitrogen desorption was not due to the products in the decomposition of the surface NH<sub>x</sub>. The broad peak at 993 K for 12MTN consisted of five peaks which appeared at 985 K (nitrogen from alumina nitrided at 973 K for 0MTN), 885 and 945 K (from MoO<sub>2</sub> and  $\gamma$ -Mo<sub>2</sub>N), 1104 K (during the transformation of  $\gamma$ -Mo<sub>2</sub>N to  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub>), and 1242 K



FIG. 1. N<sub>2</sub> desorption during TPR of ( $\bigcirc$ ) 0LTN, ( $\triangle$ ) 12LTN, and ( $\blacksquare$ ) 97LTN catalysts.



**FIG. 2.** N<sub>2</sub> desorption during TPR of ( $\bigcirc$ ) Al<sub>2</sub>O<sub>3</sub>, ( $\triangle$ ) 12.5%, ( $\square$ ) 43.0, and ( $\blacksquare$ ) 97.1% Mo/Al<sub>2</sub>O<sub>3</sub> nitrided with ammonia at 973 K.

(during the reduction of  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub> to molybdenum metal for 97MTN). The desorption of nitrogen at 885 and 945 K indicates that the ammonia treatment of 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> at 973 K produced molybdenum nitrides and that subsequent TPR nitrided the remaining molybdenum oxides and molybdenum nitrides with adsorbed NH<sub>x</sub>. Nitrogen desorption for the 1173 K nitrided Mo/Al<sub>2</sub>O<sub>3</sub> with several molybdenum loadings is shown in Fig. 3. The two peaks at 916 and 1033 K were observed for 77HTN, while a broad peak at 1020 was observed with a shoulder peak at 966 K for 12HTN. The peaks at about 1050 and 1170 K increased for



**FIG. 3.** N<sub>2</sub> desorption during TPR of ( $\bigcirc$ ) 0HTN, ( $\triangle$ ) 12HTN, ( $\Box$ ) 43HTN, ( $\bigcirc$ ) 77HTN, and ( $\blacksquare$ ) 97HTN catalysts.



FIG. 4. Nitrogen desorption deconvoluted for TPR of 12MTN catalyst.

97HTN and resulted in nitrogen desorption from molybdenum species. Furthermore, during TPR, the MTN and HTN catalysts had a high peak due to nitrogen desorption at temperatures of 1160 to 1210 K, whereas the peak for the LTN catalyst was negligible.

To clarify the relationship between HDN activity and the desorption of nitrogen from the catalysts during TPR, the peaks of nitrogen desorption were deconvoluted to six components for the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub>, according to results reported earlier (19) (Fig. 4). Six peaks of nitrogen desorption were due to adsorbed  $NH_x$  on (a)  $MoO_2$  at about 885 K, (b)  $\gamma$ -Mo<sub>2</sub>N at about 945 K, (c) alumina at about 985 K, and (d) molybdenum metal at about 1016 K, and were due to a structural change in (e) the transformation of  $\gamma$ -Mo<sub>2</sub>N into  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub> at 1104 K and (f) the reduction to  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub> to molybdenum metal at 1242 K. The amount of each nitrogen desorption for the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts is shown in Table 1. The peaks at 945 and 1104 K reached maximum values at the nitriding temperature of 973 K (12MTN), suggesting that the molybdenum species derived from the nitrogen peak at 1104 K

## **TABLE 1**

Deconvoluted Peak Area of N<sub>2</sub> Desorption in the TPR Profiles of Nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> Catalysts

$N_2$ amount/ $\mu$ mol g <sup>-1</sup> ( $N_2$ peak/K)							Correlation	
Catalyst	(a)	(b)	(c)	(d)	(e)	(f)	coefficient	
12LTN	703 (884)	71 (945)	63 (985)	1 (1022)	2 (1165)	0	0.999	
12MTN	(001) 40 (885)	(010) 157 (045)	(000) 40 (085)	138	210	75 (1242)	0.997	
12HTN	(885) (885)	(943) 113 (945)	(985) 9 (985)	(1010) 223 (1016)	60 (1104)	(1242) 111 (1242)	0.993	

was  $\gamma$ -Mo<sub>2</sub>N. The peak at 898 K reached a maximum due to the formation of molybdenum oxide at the nitriding temperature of 773 K (12LTN), but no peaks were observed for 12MTN and 12HTN. Furthermore, the peaks at about 1100 to 1250 K increased with increasing nitriding temperature due to nitrogen desorption as a result of the structural transformation of  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub> to molybdenum metal.

# Surface Species by XPS

The XPS binding energies of the Mo  $3d_{5/2}$  and  $3d_{3/2}$  lines for the 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, nitrided at various temperatures before the reaction, were determined. The XPS Mo 3d spectra were broad for the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. The XPS data indicate that the molybdenum species of the catalysts were widely distributed from Mo<sup>6+</sup> to  $Mo^0$ . These spectra of the binding energy of  $Mo 3d_{5/2}$  were deconvoluted into five doublets, with Mo  $3d_{5/2}$  binding energies lower than 232.7 eV for  $Mo^{6+}$  and higher than 227.6 eV for Mo<sup>0</sup>, i.e., the molybdenum oxidation states of the molybdenum species between the binding energies for Mo<sup>6+</sup> (binding energy, 232.7 eV; fwhm, 2.07 eV), Mo<sup>5+</sup> (231.4, 1.98 eV; 231.6 eV (24)), Mo<sup>4+</sup> (229.6, 1.87 eV; 229.7 eV (24)), Mo<sup>2+</sup> (228.5, 1.6 eV), and Mo<sup>0</sup> (227.6, 1.4 eV; 227.4 eV (22), 227.6 eV (23), 227.8 eV (26, 27)). These molybdenum species were assigned on the basis of the binding energy reported elsewhere (22, 23, 26, 27). The distribution of the molybdenum oxidation state for the nitrided 12.5%  $M/Al_2O_3$  catalysts is shown in Table 2. The Mo  $3d_{5/2}$  spectra of 227.6 and 228.5 eV have yet to be identified. Thompson and co-workers (29) assigned the Mo  $3d_{5/2}$  binding energy of the 227.8 and 228.5 eV levels in the XPS spectra of the molybdenum nitride samples to molybdenum metal and nitride ( $\delta$ +), respectively, indicating that Mo<sup> $\delta$ +</sup> is a molybdenum atom of molybdenum nitride ( $\delta$ +, probably 2+). Ozkan et al. (15) reported that the peak at 228.5 eV was assigned to  $Mo^{\delta+}$  with  $\delta < 4$ , corresponding to a molybdenum

#### TABLE 2

The Distribution of Molybdenum Oxidation State According to XPS Analysis of the 12.5%  $Mo/Al_2O_3$  Catalysts Nitrided at Several Temperatures

Nitriding	Distribution <sup>a</sup> (%)						
(K)	Mo <sup>6+</sup>	Mo <sup>5+</sup>	Mo <sup>4+</sup>	Mo <sup>2+</sup>	Mo <sup>0</sup>		
773	33.2	33.5	26.8	0	0		
873	22.1	35.0	40.4	0	0		
973	16.1	36.0	45.0	3.0	0		
1073	13.3	30.5	38.2	7.5	5.0		
1173	11.7	18.3	26.6	21.6	16.2		

<sup>*a*</sup> The relative abundance of each molybdenum oxidation state was calculated by dividing the Mo  $(3d_{2/3} \text{ and } 3d_{5/3})/\text{Al } 2p$  atomic ratio for a given molybdenum oxidation state by the total area of the Mo  $(3d_{2/3} \text{ and } 3d_{5/3})/\text{Al } 2p$  atomic ratio.

phase with a lower nitrogen coordination. They suggested that the Mo  $3d_{5/2}$  binding energy of 227.6 eV would be added as Mo<sup>0</sup> to the binding energies of the molybdenum species to archive a good fit of the curve of the XPS Mo 3d spectra. Furthermore, McGarvey and Kasztelan (30) reported a reduced molybdenum species with oxidation numbers lower than 4+ are referred to as  $Mo^{\delta+}$  and  $Mo^{0}$ . Thus, the Mo  $3d_{5/2}$  molybdenum signals at 227.6 and 228.5 eV were attributed to  $Mo^0$  and  $Mo^{2+}$ , respectively. The percentage of Mo<sup>6+</sup> decreased with increasing nitriding temperature but remained at 10% distribution even at 1173 K, probably due to the passivation of the catalysts after nitriding; the percentage was different from that of the *in situ* samples (28). McGarvey and Kasztelan (30) also reported that Mo<sup>6+</sup> and Mo<sup>4+</sup> were present even at reduction temperatures higher than 973 K for the 10.2% Mo/Al<sub>2</sub>O<sub>3</sub> catalyst based on XPS spectroscopy. The relative abundance of Mo<sup>5+</sup> and Mo<sup>4+</sup> reached a maximum at the nitriding temperature of 973 K and decreased at high temperatures.  $Mo^{2+}$  and  $Mo^{0}$ , both of which appeared at 973 and 1073 K, increased to 21.6 and 16.2%, respectively, at 1173 K. Thus, nitriding a catalyst with ammonia at higher temperatures is necessary to significantly reduce the oxidation states to  $Mo^{2+}$  and  $Mo^{0}$ . On the other hand, there were several peaks of N 1s and Mo 3p binding energies in the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts in the region of XPS N 1s from 390 to 410 eV. The XPS N 1s spectra are reported to be the binding energies at 398.1 eV (15), 397.4 eV (2), and 397.2 eV (31) (XPS N 1s binding energy for Mo-N). The peaks higher than 398.8 eV were also assigned to the N 1s levels of NH3 adsorbed on the surface Lewis acid site of the Al-ZSM-5 zeolite (32). The Mo  $3p_{3/2}$ spectra in the range of 399.4 to 393.6 eV overlapped with the N 1s spectra (33-35).

# FTIR Spectra of NH3 on Mo/Al2O3

The IR spectra of ammonia adsorbed on the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts after dosing with several pulses of ammonia in a stream of helium at 573 K (Fig. 5) were used to determine the nature of the acid sites present on the catalysts. The nitrided catalysts exhibited a strong spectrum at about 1264  $cm^{-1}$  in addition to small spectra at 1481 and 1616  $\text{cm}^{-1}$ . The band at 1264  $\text{cm}^{-1}$  was reported to be the band at 1267 cm<sup>-1</sup> attributed to the chemisorbed ammonia on the sulfided Mo/Al<sub>2</sub>O<sub>3</sub> (36, 37). The band for 12MTN and 12HTN shifted by  $6 \text{ cm}^{-1}$  from 1264 to 1258 cm<sup>-1</sup>. This result indicates that the electron-rich molybdenum surface has a low frequency because of the formation of molybdenum nitride. The bands from 1258 to 1264 cm<sup>-1</sup> are ascribed to the presence of the surface Lewis acid sites (surface-bonded species of NH<sub>3</sub>) (38-40). Although a very weak band at about 1481 cm<sup>-1</sup> was observed for Mo/Al<sub>2</sub>O<sub>3</sub>, the IR band at 1481  $\text{cm}^{-1}$  was close to the band at 1468 to 1480  $\text{cm}^{-1}$ (oxided and reduced Mo/Al<sub>2</sub>O<sub>3</sub> catalysts). The IR bands at 1450 to 1485 cm<sup>-1</sup> ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) (39, 40) were due to the



FIG. 5. Diffuse reflectance FT-IR spectra of  $NH_3$  adsorption on 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> at 553 K. B, Brønsted acidity; L, Lewis acidity.

deformational mode of  $NH_4^+$  formed by the interaction of ammonia with the Brønsted acid sites. The treatment of the 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> with ammonia demonstrated that Lewis acid sites predominate on the catalysts. The 12HTN catalyst maintained the band at 1264 cm<sup>-1</sup> without the broad band at 1481 cm<sup>-1</sup>. The spectra at approximately 1264 and 1481 cm<sup>-1</sup> were attributed to coordinated ammonia species on the Lewis acid sites and to NH<sub>4</sub><sup>+</sup> ions on the Brønsted acid sites, respectively. The IR spectra corresponding to Lewis acidity (ca. 1264 cm<sup>-1</sup>) and Brønsted acidity (ca. 1480 cm<sup>-1</sup>) for the 12HTN, 12MTN, and 12HTN catalysts are shown in Fig. 6. Lewis and Brønsted acidity decreased at higher temperatures. The 773 K nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> had 25 times more Lewis acid sites than Brønsted acid sites. The treatment with ammonia at 1173 K resulted in more Lewis acid sites but caused a slight increase in the number of Brønsted acid sites compared to the treatment at 973K. In a previous paper (41), the FTIR spectroscopy of chemisorbed pyridine on the catalysts at 573 K indicated that Lewis acidity (1264 cm<sup>-1</sup>) was predominant on the molybdenum atom of the catalysts in the absence of surface Brønsted acidity (1480 cm<sup>-1</sup>) for the nitrided and reduced 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. In the present study, however, some Brønsted acidity was observed even at the nitriding temperature of 1173 K. This can probably be explained by the same factor that was responsible for  $NH_x$  or nitrogen species remaining in the catalyst even though the catalyst was purged at 973 K after nitriding at 773 to 1173 K. This adsorbed or dissolved nitrogen species reacted with ammonia as a probe gas to regenerate the Brønsted acid sites. Fur-



**FIG. 6.** Surface ( $\bullet$ ) Lewis acidity and ( $\blacksquare$ ) Brønsted acidity of the 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalyst as a function of nitriding temperature.

thermore, molybdenum nitride would attract a hydrogen atom of ammonia to compensate for the lack of nitrogen atoms of the Mo<sub>2</sub>N structure (e.g.,  $\gamma$ -Mo<sub>2</sub>N easily releases nitrogen to form  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub>) and to polarize the hydrogen atom to a proton on molybdenum nitrides. These Brønsted acid sites might be the molybdenum oxynitrides reported by Djéga-Mariadassou *et al.* (17).

## HDN of Carbazole on Nitrided Mo/Al<sub>2</sub>O<sub>3</sub>

The time dependence of the rate of the HDN of carbazole on the 973 K nitrided catalysts at 573 K and a total pressure of 10.1 MPa is shown in Fig. 7. The nitrided catalysts deactivated rapidly during the first hour of the reaction. The HDN rate for the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub>



FIG. 7. The HDN of carbazole on the various nitrided catalysts at 573 K and 10.1 MPa.

## TABLE 3

		Catalyst <sup>a,b</sup>							
Reaction product <sup>e</sup> (%)	12LTN	12MTN	12HTN	43MTN	58MTN	77MTN	97MTN	12LTR <sup>a</sup>	
Bicyclohexyl	6.1 (6.5)	8.8 (2.8)	5.9 (3.6)	10.9	17.2	2.4	6.7	1.8	
Cyclohexylhexene <sup>d</sup>	7.9 (3.1)	9.3 (1.1)	9.2 (1.5)	2.7	4.9	0.5	0.7	2.5	
Perhydrocarbazole	0.2 (0.9)	1.0 (2.4)	19.8 (3.1)	3.5	5.0	2.2	0.5	1.4	
Decahydrocarbazole	0.9 (3.2)	0.4 (2.1)	5.8 (4.2)	3.6	6.7	1.7	2.1	2.2	
Hexahydrocarbazole	0.4 (2.3)	0.3 (1.9)	8.5 (2.5)	1.6	2.7	1.9	2.7	0.5	
Tetrahydrocarbazole	23.5 (18.3)	22.2 (8.8)	15.3 (8.6)	17.9	43.6	12.3	28.1	16.5	
Carbazole	61.0 (65.7) <sup>e</sup>	58.0 (80.9) <sup>e</sup>	35.5 (76.5) <sup>e</sup>	59.9	19.9	79.0	59.2	75.1	
Conversion (%)	39.0 (34.3)	42.0 (19.1)	64.5 (23.5)	40.1	80.1	21.0	40.8	24.9	

Product Distribution in the HDN of Carbazole on the Nitrided Mo/Al<sub>2</sub>O<sub>3</sub> Catalysts at 573 K and a Total Pressure of 10.1 MPa

<sup>*a*</sup> Cooled with NH<sub>3</sub>: The nitrided catalysts were cooled from the nitriding temperature to room temperature in a stream of ammonia.

<sup>b</sup> (Parentheses) Cooled with He: The nitrided catalysts were purged with helium for 1 h at 973 K and cooled from the nitriding temperature to room temperature in flowing helium.

 $^{\circ}$ 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> was reduced in a hydrogen flow of 11.2  $\mu$ mol s<sup>-1</sup> for 3 h at 673 K.

<sup>*d*</sup>Cyclohexylhexene and cyclohexylbenzene.

<sup>e</sup>Reaction products with a boiling point lower than that of xylene were not calculated.

catalyst was 0.736  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup> 0.5 h after the start of the run and decreased to 0.34  $\mu$ mol h<sup>-1</sup> m<sup>-2</sup> after 3 h (almost the same concentration at 9 h). The product distribution of carbazole HDN on the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts from 7 to 9 h is shown in Table 3. The major reaction products were bicyclohexyl and tetrahydrocarbazole. Hydrogenated carbazole compounds, such as hexahydrocarbazole and octahydrocarbazole, were observed in small amounts, in contrast to tetrahydrocarbazole. Relatively large amounts of perhydrocarbazole were formed for the 12HTN catalyst, indicating a high selectivity for hydrogenation compared to that of 12MTN. The 12HTN catalyst, which contained molybdenum metal, was most active during the hydrogenation of carbazole. The 12LTN catalyst was much less active than the other nitrided catalysts for carbazole HDN. Accordingly, a plausible reaction scheme for the HDN of carbazole is shown in Fig. 8. Carbazole was successively hydrogenated to perhydrocarbazole on the nitrided catalyst as well as on the reduced and sulfided catalysts (25, 42). Bicyclohexyl was produced during the C-N hydrogenoly-

sis of perhydrocarbazole after the consecutive hydrogenation of carbazole to perhydrocarbazole. Cyclohexylbenzene and cyclohexylcyclohexene were probably formed from the C-N bond scission of hexahydrocarbazole and decahydrocarbazole, respectively, although decahydrocarbazole was not detected in the reaction products. Since the carbazole HDN over the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts contained small amounts of these compounds, the nitrided catalysts effectively decreased the nitrogen content which promoted selective C-N hydrogenolysis of partially hydrogenated compounds with reduced hydrogen consumption. In a previous paper (3, 42), the data on the HDN of carbazole on 12.5%Mo/Al<sub>2</sub>O<sub>3</sub> nitrided at 773 K were collected in two separate experiments using the nitrided catalyst with two average particle sizes  $(d_i)$  of 1.275 (0.85 to 1.70) and 0.605 (0.5 to 0.71) mm at temperatures of 553 to 633 K and a constant partial pressure of carbazole and hydrogen. When the reaction was limited by interpolate mass transfer, the C-N hydrogenolysis rate (*r*<sub>i</sub>) varied inversely with particle size;  $r_{\rm i} \propto 1/d_{\rm i}$  (43). The ratios of  $r_1/r_2$  were independent for the



FIG. 8. Reaction scheme of the HDN of carbazole on the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts.

#### **TABLE 4**

			CO adsorbed			
Catalyst	Surface area $(m^2 g^{-1})$	Total	Irrevers	ible	HDN rate <sup>a</sup> ( $\mu$ mol m <sup>-2</sup> h <sup>-1</sup> )	${ m TOF}^b$ (h <sup>-1</sup> )
		$(\mu \text{mol g}^{-1})$	$(\mu \text{mol g}^{-1})$	$10^{12}/cm^{-2}$		
12LTN	$226^{c} (223)^{d}$	$38.8^c (23.6)^d$	$6.99^c (5.43)^d$	1.87 <sup>c</sup>	$0.654^c (0.478)^d$	21.1 <sup>c</sup> (19.6) <sup>d</sup>
12MTN	195 (183)	18.2 (8.2)	3.18 (1.59)	0.988	0.736 (0.622)	45.1 (71.6)
12HTN	138 (132)	10.5 (23.0)	1.28 (4.8)	5.67	0.971 (0.864)	104.7 (23.8)
43MTN	64	52.0	28.1	26.4	1.79	4.08
58MTN	91	44.6	20.3	13.4	1.01	4.53
77MTN	39	7.90	6.50	10.0	2.49	14.9
97MTN	33	84.4	43.8	79.9	2.88	2.17
12LTR <sup>e</sup>	250	7.80	4.60	1.11	0.539	29.3

Hydrodenitrogenation of Carbazole on the Nitrided Mo/Al<sub>2</sub>O<sub>3</sub> Catalyst at 573 K

<sup>a</sup> HDN rate is based on the rate of disappearance of carbazole.

<sup>b</sup> TOF is the HDN rate at 0.5 h ( $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>) divided by the irriversibly adsorbed CO ( $\mu$ mol g<sup>-1</sup>).

 $^{c,d,e}$  See the respective footnotes  $(^{a,b,c})$  in Table 3.

 $^{c}$  The surface areas of Al<sub>2</sub>O<sub>3</sub> nitrided at 773, 973, and 1173 K are 155, 131, and 108 m<sup>2</sup> g<sup>-1</sup>, respectively.

catalyst particle sizes at the reaction temperatures of 573 to 633 K. From these results, the effect of external mass transport was expected to be negligible.

In a series of catalysts nitrided at 973K, the 12MTN catalyst showed the lowest HDN rate while the 97MTN catalyst showed the highest HDN rate. The 12HTN catalyst in the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts showed a high HDN rate. The CO adsorption of the catalysts is shown in Table 4. The ratios of the total amount of CO adsorption to the irreversible amount for the 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts are greater than those for the 43.0 to 97.1% MTN catalysts. The amount of irreversible CO uptake for the 12MTN catalyst was  $1.0 \times 10^{12}$  molecules cm<sup>-2</sup>, which was half that of the 12LTN catalyst and 0.2 that of the 12HTN catalyst. According to Monte Carlo simulation, CO adsorbed on molybdenum atoms and nitrogen-deficient sites (molybdenum atoms at the second layer) on the top layer of (111) phase  $\gamma$ -Mo<sub>2</sub>N (44). Furthermore, previous studies (25, 42) showed that the hydrogenation of carbazole to tetrahydrocarbazole was not fully equilibrated at 573 K in the HDN of carbazole and that the C-N hydrogenolysis rate (the formation of bicyclohexyl) was a determining step about at least 593 K. The TOF was calculated by dividing the HDN rate (disappearance rate) by the amount of CO uptake, that is, the activity of each active site of the nitrided catalysts representing the hydrogenation of carbazole. The order of the TOF of the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts was the same as that of the HDN rate as based on the surface area of the catalyst (Table 4). The TOF (45.1  $h^{-1}$ ) of the 12MTN catalyst was about 0.4 times more active than the 12HTN catalyst and about twice as active as the 12LTN catalyst. Thompson *et al.* (6) reported the TOF of  $11.9 \text{ h}^{-1}$  for quinoline HDN at 663 K for 100% Mo<sub>2</sub>N nitrided at 973 K based on the titration of sites with CO. They obtained a TOF that

is 5.5 times greater than that  $(2.17 \text{ h}^{-1})$  in our experiment on carbazole HDN on the 97MTN catalyst at 573 K. Thus, the TOF of the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was approximately 2 to 100  $h^{-1}$  for the HDN of carbazole at 573 K and a total pressure of 10.1 MPa. Table 4 shows that the ammonia-cooled LTN and HTN catalysts were more active than the helium-cooled catalysts (Bracket). Before the nitrided catalysts were passivated with 1% O<sub>2</sub> in He for 12 h, the catalysts were cooled from the nitriding temperature to room temperature in a stream of ammonia. Adsorbed  $NH_{r}$ and dissolved nitrogen formed. In this post treatment, the NH<sub>x</sub> species was associated with oxygen atoms in the catalysts and probably led to the generation of the Brønsted acid sites and to high activity for the HDN reaction. On the contrary, when the 12MTN catalyst was purged with helium and cooled to room temperature in a stream of helium, adsorbed  $NH_x$  and dissolved nitrogen in the catalyst were removed. For helium-cooled 97MTN,  $\gamma$ -Mo<sub>2</sub>N was transformed to  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub> and was less active than  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub> for the hydrogenation in the HDN of carbazole (19). Thus, the helium-cooled 12MTN catalyst was more active than the ammonium-cooled catalyst. Furthermore, the 973 K nitrided catalysts with higher molybdenum loadings were less active than the 12MTN catalyst. The 97MTN catalyst had the lowest TOF activity. Since the molecular size of carbazole is larger than that of CO despite a large number of irreversible CO adsorbed on the 97MTN catalyst (Table 4), all the adsorption sites of CO were not used for the adsorption of carbazole involving carbazole HDN. In addition, the 97MTN catalyst may have created some molybdenum atoms with high crystallinity on the surface, different from the molybdenum species interacted with alumina on the surface of the 12MTN catalyst. Therefore, the TOF of the 97MTN was lower than that of the 12MTN.

## Active Molybdenum Species in Carbazole HDN

The TOF for the HDN of carbazole is plotted versus the distribution of the molybdenum oxidation state of the 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalysts obtained from the XPS analysis (Fig. 9). The TOF for carbazole HDN (hydrogenation) was linearly correlated with the distribution of both Mo<sup>2+</sup> and Mo<sup>0</sup> on the catalysts. Based on the XPS study, the 1173 K nitrided catalyst had more oxidation states of Mo<sup>2+</sup> and Mo<sup>0</sup> compared to the other catalysts nitrided at the lower temperatures. Hydrogenation activity increases with a decreasing distribution of the fractions of Mo<sup>4+</sup> and Mo<sup>3+</sup>. The distribution of Mo<sup>6+</sup> ions decreased from 33 to 12%, corresponding to an increase in TOF from 21.1 to 104.7  $h^{-1}$ , respectively. This result indicates that Mo<sup>2+</sup> and Mo<sup>0</sup> are active centers for hydrogenation in carbazole HDN on the nitrided Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Bussell et al. (45) studied the infrared spectroscopy of adsorbed CO on a molybdenum nitride catalyst and deduced that Mo<sup>2+</sup> sites were present on the surface of the molybdenum nitride. Sullivan and Ekerdt (46) also reported that  $Mo^{2+}$  was the most active molybdenum species of the sulfided silica-supported molybdenum catalysts for thiophene HDS. Furthermore, Yamada et al. (27) reported that both  $Mo^{2+}$  and molybdenum metal were active during the hydrogenation of benzene with the former being more active. Molybdenum metal is probably partially formed as patches of molybdenum metal on the molybdenum nitrides or on the reduced molybdenum oxide. Therefore, the 12HTN catalyst had patches of molybdenum metal on its surface which were highly active for the hydrogenation in the HDN of carbazole. When the catalyst was placed in a stream of ammonia and cooled from the nitriding temperature to room temperature after nitriding, excess ad-



Distribution of Mo oxidation states [%]

**FIG. 9.** The relationship between the TOF for carbazole HDN and the molybdenum oxidation state of the nitrided catalysts obtained from the XPS analysis.



**FIG. 10.** The relationship between the TOF for carbazole HDN and nitrogen desorption ((*d*) at 1016–1022 K) during TPR.

sorbed ammonia and NH<sub>x</sub> reacted with hydrogen during TPR to form nitrogen. The TPR study of N<sub>2</sub> desorption gave more acceptable results than the study on ammonia adsorption as far as the nature of the acid sites on the nitrided catalysts for carbazole HDN is concerned. Figure 10 is the TOF of the nitrided catalyst as a function of nitrogen desorption during TPR. The TOF for the carbazole HDN was related to nitrogen desorption at 1016 K. The nitrogen desorption at 1016 K is due to the nitrogen release from the surface NH<sub>x</sub> on molybdenum metal. According to the TPR study, therefore, the molybdenum metal on the surface of 12HTN and 12MTN had the highest TOF for the hydrogenation in the HDN of carbazole. Furthermore, the TOFs of both the helium- and the ammonia-cooled catalysts in the HDN (hydrogenation) of carbazole increased at nitriding temperatures from 773 to 1173 K (Table 4). However, the peak area of the IR spectra of Lewis and Brønsted acidity clearly decreased from the nitriding temperature of 773 to 1173 K, even though the catalysts were purged with helium to eliminate excess nitrogen species for the infrared spectroscopy. Therefore, the TOF of the helium-cooled 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> did not coincide with the number of Lewis and Brønsted acid sites, except for the increased ratio of Lewis/Brønsted acidity. The activity of the nitrided catalysts for the hydrogenation in the carbazole HDN in this study is not related to surface acidity but rather to the reduced molybdenum ions Mo<sup>2+</sup> and Mo<sup>0</sup> on the surface of the molybdenum nitride catalysts.

# CONCLUSIONS

1. This paper revealed mainly the active sites for the hydrogenation in the hydrodenitrogenation of carbazole on a basis on TOF, TPR, XPS, and IR. 2. The TPR experiments showed that the desorption of nitrogen gas from the nitrided 12.5% Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was deconvoluted into six peaks: the nitrogen peak from adsorbed NH<sub>x</sub> on (a) MoO<sub>2</sub>, (b)  $\gamma$ -Mo<sub>2</sub>N, (c) alumina, and (d) molybdenum metal, from the transformation of (e)  $\gamma$ -Mo<sub>2</sub>N into  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub>, and the reduction from (f)  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub> to molybdenum metal.

3. The TOF value was calculated by the HDN rate (conversion of carbazole) divided by the irreversible CO adsorbed on the active sites such as molybdenum atoms and nitrogen-deficient sites on the top layer surface.

4. The ammonia-cooled 12HTN and helium-cooled 12MTN catalysts exhibited the highest activity (TOF) for the hydrogenation in the carbazole HDN.

5. The TOF of the catalysts was related to nitrogen desorption due to the release of nitrogen from the surface  $NH_x$  on molybdenum metal, indicating that molybdenum metal is created on the surface of the catalysts.

6. XPS analysis showed that TOF is correlated to the distribution of  $Mo^{2+}$  and  $Mo^{0}$  in the nitrided catalysts, suggesting that  $Mo^{2+}$  and  $Mo^{0}$  are active centers for the hydrogenation in the HDN of carbazole.

7. The activity of the nitrided catalysts for the hydrogenation in carbazole HDN is not related to surface acidity but rather to the reduced molybdenum ions  $Mo^{2+}$  and  $Mo^{0}$ on the surface of the molybdenum nitrided catalysts.

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