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TPD study and carbazole hydrodenitrogenation activity of nitrided molybdena–alumina

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Abstract

The relationship between the activity and surface molybdenum species of nitrided 12.5% MoO_3/Al_2O_3 was studied in the hydrodenitrogenation (HDN) of carbazole at 573 K and 10.1 MPa total pressure. The surface molybdenum species were determined by the desorption of nitrogen gas during TPD. The surface area of NH_3-cooled Mo/Al_2O_3 nitrided at 773 and 1173 K was decreased by 8% and 61% from 245 $m^2 g^{-1}$ of the fresh MoO_3/Al_2O_3, respectively. The NH_3-cooled Mo/Al_2O_3 catalysts had slightly higher surface area than the He-cooled catalysts. The HDN rate increased with increasing nitriding temperature in the HDN of carbazole on the nitride catalysts. The NH_3-cooled Mo/Al_2O_3 catalysts nitrided at 1173 K were the most active in carbazole HDN and the He-cooled catalyst nitrided at 773 K was the least. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Carbazole; Hydrodenitrogenation; Molybdenum nitride; Temperature-programmed desorption

1. Introduction

The catalytic properties of unsupported Mo nitrides are governed by their bulk composition and surface structure. The synthesis and catalytic property of the Mo nitrides have been studied extensively. Recently, alumina-supported Mo nitrides with low loading, large surface area, strong mechanical resistance, and easy molding and manufacturing of catalysts have been developed for industrial application. The alumina-supported Mo nitrides were applied to hydrodenitrogenation (HDN) and hydrodesulfurization [1–3]. The activity of the supported Mo nitride was superior to that of a commercial sulfided Ni–Mo hydrotreating catalyst for the HDN of pyridine [1]. A nitrided Mo/Al_2O_3 catalyst was reported to be about three times more active than the sulfided and reduced Mo/Al_2O_3 catalyst in the HDN of carbazole [2]. However, much less attention has been given to examining the surface structure and composition of the catalysts such as Mo and nitrogen species adsorbed on the surface of the alumina-supported Mo nitrides. Few studies have been reported on the effect of these species on a treatment in flowing NH_3 or He gas during cooling to room temperature after nitridation of molybdena–alumina precursor.

Temperature-programmed desorption (TPD) is a useful technique for determining the presence of

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organic compounds adsorbed on catalyst surface and illustrates the value of detailed analysis of the products evolved from the surface of catalysts [4–6]. The application of this technique is demonstrated here for nitrided 12.5% MoO_3/Al_2O_3, which exists in oxidic, nitrided and metal forms on alumina and forms such products as water, ammonia, nitrogen, and hydrogen. These gas products can characterize the Mo and nitrogen species on the surface. In this work, the surface nitrogen species are determined by TPD for the 12.5% MoO_3/Al_2O_3 treated with NH_3 at 773, 973, and 1173 K, followed by either cooling in He or in NH_3 after purging. The effect of nitriding treatment on the surface Mo and nitrogen species of the catalysts is determined. The relationship between the molybdenum species and the activity of the nitride Mo/Al_2O_3 catalyst for the HDN of carbazole at 573 K and 10.1 MPa total pressure is also discussed.

2. Experimental

Hydrogen and helium (99.999%) were dried by passing them through Deoxo units (SUPELCO) and a Linde 13X molecular sieve trap prior to use. NH_3 (99.999%) was used without further purification. 12.5% MoO_3/Al_2O_3 (Nikki Chemical) was prepared by mixing ammonium paramolybdate with γ-alumina and molded into 3 mm o.d. pellets with a kneader. The 12.5% MoO_3/Al_2O_3 was packed on a fritted plate in a quartz microreactor, treated with pure NH_3 at 49.6 μmol s^{-1} from 573 to 773, 973 and 1173 K at a rate of 0.0167 K s^{-1}, and held at this temperature for 3 h. After nitriding, two alternative treatments were performed. In the first, the nitrided catalyst was cooled from the nitriding temperature to room temperature in flowing NH_3. In the second treatment, the nitrided catalyst was purged at 973 K in flowing He for 1 h after nitriding and then cooled to room temperature in flowing He. For the TPD experiment, the nitrided catalyst was heated in situ to 373 K 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 helium flow of 11.1 μmol s^{-1}. The gases desorbed from the catalyst were monitored on-line using a quadrupole mass spectrometer. The desorption rates of H_2, N_2, NH_3 and water were calculated by calibration curves for each gas. Abbreviated notations of the nitrided catalyst are used throughout this paper as follows: 12NH-L denoted 12.5 wt% Mo/Al_2O_3 nitrided at 773 K in flowing NH_3 for 3 h, followed by cooling to room temperature in flowing NH_3, while 0HE-H denotes Al_2O_3 which was purged with He at 973 K for 1 h and cooled to room temperature in flowing He after nitriding 1173 K in flowing NH_3 for 3 h. The HDN of carbazole on the nitrided 12.5% Mo/Al_2O_3 catalyst (2.0 g, 10–20 mesh) was conducted at 573 K and 10.1 MPa in a fixed-bed microreactor using 0.25 wt% carbazole in xylene. Reaction products were quantitatively analyzed using an FID gas chromatograph with 2% Silicone OV-17. The rate of carbazole HDN was calculated by conversion of carbazole. The specific surface area of the catalyst was measured by nitrogen adsorption using a standard volumetric BET apparatus after evacuation of the sample at 473 K and 10^{-2} Pa for 2 h. Molybdenum analysis was done using atomic absorption spectroscopy.

3. Results and discussion

3.1. BET surface area

The surface areas of the NH_3- and He-cooled Mo/Al_2O_3 catalysts are shown in Table 1. The surface area of the 12NH catalyst decreased with increasing nitriding temperature. The surface area of 226 m^2 g^{-1} was obtained for the 773 K-nitrided catalyst. The surface area of the 12NH-L and -H was decreased by 8% and 61% from 245 m^2 g^{-1} of the fresh MoO_3/Al_2O_3, respectively. From the result, higher nitriding treatment lowered the surface area of the catalysts. The surface areas of the 12NH catalysts were slightly larger than those of the 12HE catalysts. This is probably because cooling of the nitrided catalysts with NH_3 increased the surface area to form smaller catalyst particles with increased surface heterogeneity when compared with helium gas cooling.

3.2. TPD of nitrided 12.5% MoO_3/Al_2O_3 and Al_2O_3

The TPD profile for the 12NH and 0NH catalysts is shown in Fig. 1. Two different types of desorption peaks were observed in profiles of N_2 desorption; the temperature region of 815–845 K and above 960 K. The first is a large desorption peak of N_2, accompanied

Table 1
The results of TPD and HDN of carbazole on the catalysts

Catalyst[a] nitriding temperature (K)	BET (m^2 g^{-1})		HDN[d] (μmol h^{-1} m^{-2})			Total N_2[e] desorbed (mmol g^{-1})	
	NH[b]	HE[c]	NH	HE	NH/HE ratio	NH	HE
773	226	223	0.24	0.230	1.04	2.11	0.167
973	195	183	0.318	0.277	1.15	1.0	0.302
1173	138	132	0.821	0.741	1.11	1.03	0.341

[a] Fresh (12.5% MoO_3/Al_2O_3): 245 m^2 g^{-1}.
[b,c] NH was cooled in NH_3 to room temperature, and HE in He to room temperature after the sample was purged at 973 K for 1 h in He.
[d] Based on conversion of carbazole in carbazole HDN at 573 K and 10.1 MPa.
[e] N: on a basis of N_2 desorbed during TPD.

by H_2 at temperatures of 815–845 K. The intensity of the desorption peaks decreased with increasing nitriding temperature. The desorption peaks of N_2 and H_2 were observed for the 12NH catalysts, in agreement with those obtained from NH_3 cooling of the unsupported sample (γ-Mo_2N) [4]. This is due to the release of N_2 and H_2 during the decomposition and recombination of NH_x adsorbed on the Mo species during TPD. The molar ratio of H_2/N_2 was 2, 2, and 1 for the 12NH-L, -M, and -H catalysts, respectively, indicating the presence of the NH_2 and NH species on the surface of the catalysts. Haddix et al. [5] also reported that adsorbed NH_3 decomposed above 573 K by process of sequential dehydrogenation to produce NH_2 and NH groups as well as atomic N and H atoms. The tailing peak of N_2 and H_2 desorption for the 12NH catalysts was originated from those of the 0NH (Fig. 2(a)–(c)) with less hydrogen at about 950 K. In contrast, for the 12HE catalysts, the desorption of N_2 and H_2 gases were observed much less than those for the 12NH catalysts as shown in Fig. 1(d)–(f). This result showed that purging of the nitride catalysts in flowing He at 973 K removed most of all NH_x species adsorbed on the catalysts below about 1000 K. Therefore, the desorption peak of N_2 and H_2 at about 840 K is attributed to the release of N_2 and H_2 during the decomposition and recombination of NH_2 and NH species on the surface of the 12NH catalysts. Furthermore, a slight formation of H_2O at 820 K for the 12NH-L catalyst indicated that Mo oxides were present on the catalysts and further reduced and nitrided with adsorbed NH_x on the surface during TPD. The presence of Mo oxides on the 12NH-L catalyst is probably due to a strong interaction between the Mo species and alumina.

The second type of N_2 desorption is represented by the broad peaks above 960 K, for the NH and HE catalysts. This is in accordance with the release of N_2 above 950 K during the transformation of γ-Mo_2N to β-$Mo_2N_{0.78}$ in the NH and HE catalysts and the reduction of β-$Mo_2N_{0.78}$ to Mo metal of the HE-M, HE-H and NH-H of the unsupported molybdenum nitrides [7]. The N_2 desorption was also observed above 960 K, due to the release of N_2 from adsorbed nitrogen on γ-Mo_2N and MoO_2 in the NH catalysts. In previous papers [4,7], nitriding MoO_3 with NH_3 at 773 K formed MoO_2, which in turn formed γ-Mo_2N in the treatment at 973 K. The as-prepared 1173 K-nitrided sample contained mainly Mo metal with a small amount of β-$Mo_2N_{0.78}$. Nitriding treatment resulted in forming different Mo species on the catalyst. Furthermore, purging the 973 K-nitrided as-prepared sample after nitriding changed γ-Mo_2N to β-$Mo_2N_{0.78}$ for the unsupported catalyst [7]. Consequently, different Mo species are generated on the surface of the catalysts by varied nitriding and purging treatments of 12.5% Mo/Al_2O_3 catalysts, in agreement with the Mo species of the unsupported catalysts [7]. The following Mo species are likely to be present on the surface of the 12.5% Mo/Al_2O_3: Mo oxides interacted with alumina on the 773 K-nitrided catalysts, Mo oxides interacted with alumina and γ-Mo_2N on the 973 K-nitrided catalyst, and Mo nitrides and metals on the 1173 K-nitrided catalysts.

3.3. *HDN activity and Mo species*

The major denitrogenated product was bicyclohexyl with small amounts of cyclohexylhexene and hexylcyclohexane. The hydrogenated product was

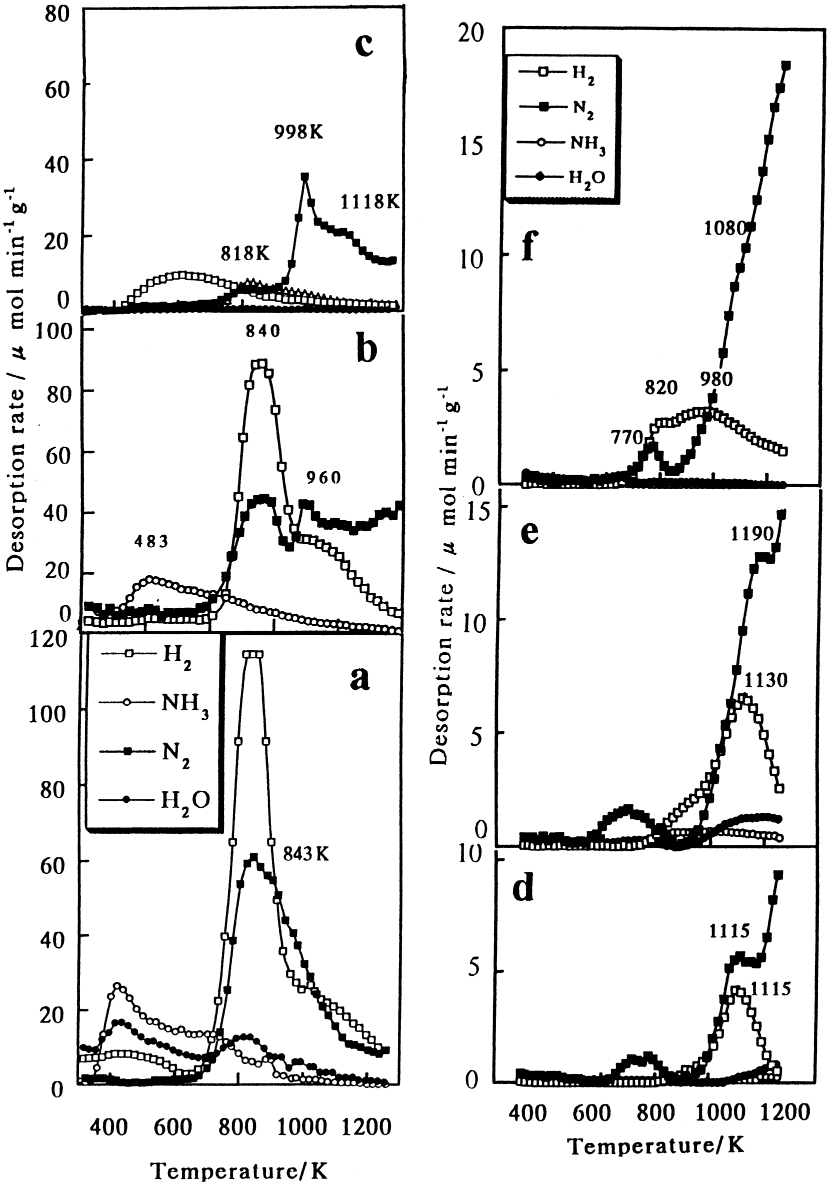

Fig. 1. TPD profiles of: (a) 12NH-L, (b) 12NH-M, (c) 12NH-H, (d) 12HE-L, (e) 12HE-M, and (f) 12HE-H.

tetrahydrocarbazole in the HDN of carbazole. Other hydrogenated carbazole compounds such as hexahydrocarbazole, octahydrocarbazole, and perhydrocarbazole were barely observed in the reaction products. The rate of the HDN of carbazole is given in Table 1. The HDN rate for the 12NH catalysts was greater than that for the 12HE catalysts. The 12NH-H and 12HE-H catalysts were more active than the other catalysts for the HDN of carbazole. Since the presence of NH_x adsorbed on the surface of the NH catalysts pulverizes Mo nitrides and oxides with small particle size, the NH catalyst has small particles of Mo nitrides and oxides, compared with the corresponding HE catalyst. The NH catalyst was more active than the

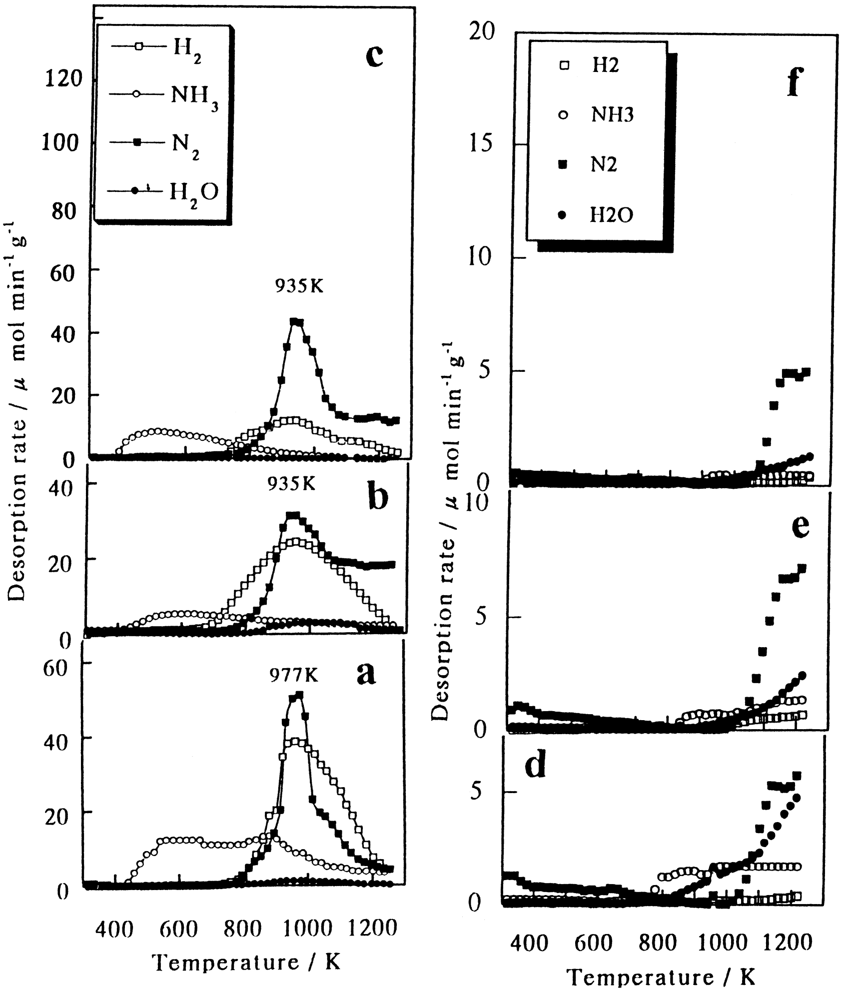

Fig. 2. TPD profiles of: (a) 0NH-L, (b) 0NH-M, (c) 0NH-H, (d) 0HE-L, (e) 0HE-M, and (f) 0HE-H.

HE catalyst for the nitrogen removal in carbazole HDN.

Bell and coworkers [8] reported that H_2 adsorption occurred at nitrogen-deficient patches of Mo present on the nitride surface. Colling and Thompson [1] also reported that the most active sites for pyridine HDN were located at perimeters of two-dimensional, raft-like domains; regions near the perimeter were also nitrogen deficient. In Table 1, the total amount of N_2 deposition decreased as follows: 12NH-L>12NH-H>12NH-M>12HE-H>12HE-M>12HE-L. However, since the 12NH-H and 12HE-H catalysts were highly active for HDN of carbazole, there is no observable relationship between the HDN activity and nitrogen deficiency. The 1173 K-nitrided catalyst was likely to be incompletely reduced Mo oxides and nitrides to Mo metals, although the 1173 K-nitrided catalysts were conceived to shrink and sinter after NH_3 treatment. The 1173 K-nitrided catalyst was expected to have patches of Mo metal species formed on its surface, which was highly active for the HDN of carbazole. Mo nitrides of the 973 K-nitrided catalyst exhibited the second highest activity in the HDN of carbazole. Moreover, since molybdenum oxides were produced on the surface of the 12.5% MoO_3/Al_2O_3 nitrided at 773 K [4], the molybdenum oxides were not as active as Mo metals and nitrides for HDN of carbazole.

4. Conclusions

1. TPD experiments indicated that NH_x species are present on the surface of the nitrided catalysts and reacted with Mo oxides and nitrides to evolve N_2 and H_2. The NH_x species were formed when cooled to room temperature with NH_3 after nitriding.
2. Purging of the nitrided catalysts in flowing He removed NH_x species adsorbed on the catalysts, whereas cooling in flowing NH_3 increased slightly the surface area by forming smaller particles and increasing the heterogeneity of the surface than that in flowing He gas.
3. The activity of 12NH and 12HE catalysts increased with increasing nitriding temperature. The 1173 K-nitrided catalyst was highly active for HDN of carbazole, and was expected to have patches of Mo nitrides and metals on the surface.

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