

Molybdenum Nitride Catalysts

II. H₂ Temperature Programmed Reduction and NH₃ Temperature Programmed Desorption

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The surface chemistries of a series of Mo nitride catalysts with surface areas ranging up to 193 m²/g were characterized using thermal desorption spectroscopies. These materials were prepared by the temperature programmed reaction of MoO₃ with NH₃. The passivated catalysts contained up to one monolayer of oxygen on or in the surface. This oxygen was removed as H₂O via two pathways during temperature programmed reduction: (a) reaction with hydrogen from decomposed NH₃ and hydrogen residue left on the surface after synthesis at temperatures less than ~550 K and (b) reaction with gas phase H₂ at higher temperatures. Nitrogen and/or surface NH_x species also reacted with gas phase H₂ producing NH₃. The NH₃ adsorption capacities were different for each of the reduced Mo nitrides; however, other variations in the temperature programmed desorption spectra were qualitatively similar. At low coverages, all of the NH₃ decomposed and the products desorbed as H₂ at 500–700 K and N₂ above 600 K. Following saturation of the surface, most of the NH₃ desorbed molecularly at 300–500 K and the balance decomposed. The ratio of molecularly desorbed to decomposed NH₃ was approximately 3 : 1 for all the catalysts suggesting a connection between the desorption and decomposition of NH₃. We have interpreted the results, in particular for the high surface area materials where the saturation coverage was low, in terms of localized NH₃ adsorption perhaps forming islands at high coverage. The pyridine HDN reaction rate increased linearly with the amount of NH₃ chemisorbed. The corresponding turnover frequency was $4.1 \times 10^{-4} \text{ s}^{-1}$ at 633 K. Finally, the number of types of NH₃ and H₂ desorption sites was a function of the surface area. The low surface area, high activity Mo nitrides possessed low and high temperature desorption sites. Only the low temperature sites were observed for the high surface area, low activity materials. The rate limiting step for NH₃ desorption from the Mo nitrides was first order with desorption energies for the low and high temperature sites of 24 ± 4 and 32 ± 5 kcal/mol, respectively. © 1996 Academic Press, Inc.

INTRODUCTION

Molybdenum nitrides are active and selective hydrodenitrogenation (HDN) (1–5) and hydrodesulfurization

(HDS) (6–8) catalysts. These materials can be prepared in high surface area form (>150 m²/g) by reacting MoO₃ with NH₃ while heating the mixture linearly in a temperature programmed manner. Previously we described the influence of the synthesis conditions on the surface areas (9) and HDN activities (3) of Mo nitrides. We have also described in some detail the surface and bulk structural and compositional properties of these materials (9, 10). A brief description of the results is given in the next paragraph.

Molybdenum nitrides with surface areas ranging up to ~200 m²/g were prepared and characterized. The materials were highly active for pyridine HDN. Their activities on an oxygen uptake basis were superior to those of sulfided Ni–Mo/Al₂O₃ and Co–Mo/Al₂O₃ catalysts. Variations in the activity with changes in the surface area suggested that there were variations in the surface structure and composition. Table 1 lists pertinent surface properties for the Mo nitrides. Their primary bulk crystalline phase was γ -Mo₂N (fcc); however, the near-surface was body-centered. This result coupled with those from X-ray photoelectron spectroscopy was consistent with the surface consisting of a body-centered oxynitride. There was not a clear connection between the surface structure or composition and the catalytic properties; however, we do find a strong correlation between the surface chemistry and catalytic activity. For example, the hydrogen binding, based on H₂ temperature programmed desorption (TPD), was weakest for the most active catalysts (3).

In this paper we relate results from H₂ temperature programmed reduction (TPR) and NH₃ TPD to the pyridine HDN activities of the Mo nitrides briefly described in the last paragraph. Hydrogen and NH₃ are of interest because they play key roles in HDN. Haddix *et al.* (11) used proton NMR to characterize NH₃ adsorption on γ -Mo₂N. They reported that adsorption at 298 K produced weakly and strongly chemisorbed NH₃ species. At higher temperatures the weakly bound NH₃ desorbed while the more strongly bound NH₃ decomposed. Species formed during NH₃ decomposition were NH₂, NH, and atomic nitrogen and hydrogen. These results were for a material with 100 m²/g

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TABLE 1

Sorpitive, Catalytic, and Compositional Properties of Mo Nitrides

Sample	Surface area (m ² /g)	O ₂ uptake ^a (μmol O ₂ /g)	HDN activity ^b (pmol/m ² /s)	N/Mo ^c	O/Mo ^c
MoN-A	193	206	89.6	—	—
MoN-B	116	112	403	0.60	0.20
MoN-C	52	93	927	0.63	0.11
MoN-D	39	58	2220	1.00	0.16
MoN-E	28	54	1690	1.22	0.10
MoN-F	24	67	2180	0.48	0.18
MoN-G	12	24	1340	1.11	0.14
MoN-H	4	7	3540	0.91	0.13

^a Measured at 195 K.

^b Measured in 0.6% pyridine/H₂ at 633 K and 101 kPa.

^c Measured for reduced materials using X-ray photoelectron spectroscopy (10).

whose surface was saturated with NH₃. Given the reported changes in catalytic properties with variations in the surface area, we decided to examine γ -Mo₂N powders with a range of surface areas. Molybdenum nitrides are usually passivated after synthesis in a dilute mixture of O₂ and the resulting passivation layer must be removed prior to their use as catalysts. The passivated catalyst is most often activated by reduction in H₂ (1, 12). We used H₂ TPR to investigate the processes involved in reduction of the passivation layer.

EXPERIMENTAL

Catalyst Preparation

Details of the synthesis and structural characterization have been reported elsewhere (9, 10) and will only be summarized here. The catalysts were prepared by flowing NH₃ over a bed of MoO₃ powder while increasing the reaction temperature linearly. Following the temperature program, the materials were cooled to room temperature in NH₃ and passivated in 1% O₂ in He to inhibit bulk reoxidation. The predominant bulk phase produced was γ -Mo₂N although very small amounts of Mo were present in the two lowest surface area catalysts, MoN-G and MoN-H. Prior to the sorption and activity measurements, the materials were reduced for at least 3 h in flowing H₂ at 673 K. Surface areas were measured using the standard BET method. Pulsed oxygen chemisorption (pulses of 9.98% O₂ in He) was carried out at 195 K. The pyridine HDN activities were measured using a feed stream of 0.60% pyridine in H₂ at atmospheric pressure and temperatures between 588 and 648 K.

Thermal Desorption Spectroscopy

The H₂ TPR and NH₃ TPD experiments were performed using an Altamira AMI-M which was retrofitted with a Fisons Sensorlab 200D mass spectrometer. Between 50 and 250 mg of catalyst was placed in a Pyrex U-tube on

a quartz wool plug. The thermocouple was placed in the bed to insure accurate measurement and control of the catalyst temperature. To distinguish peaks due to reduction of the materials from those due to outgassing, the passivated Mo nitrides were heated from room temperature to 773 K at 15 K/min in Ar (Air Products, 99.998%, with Matheson Gas Purifier Model 6406) flowing at 30 cm³/min. Note that the maximum safe operating temperature for our TPD/TPR system was 773 K. This temperature should be sufficient to characterize the adsorption of NH₃ on Mo nitride surfaces (11). The TPR experiments consisted of heating the passivated Mo nitrides from room temperature to 773 K at 15 K/min in 5.2% H₂ in Ar (Scott, CMG) flowing at 30 cm³/min and holding them at 773 K for 0.5 h. The reactor effluent was monitored using a thermal conductivity detector (TCD) and the mass spectrometer. The mass spectrometer was tuned to monitor the $m/e = 2, 14, 15, 16, 18, 28, 30, 32, 36, 44,$ and 46 signals.

Before adsorbing NH₃, the passivated materials were reduced at 673 K in H₂ (Scott, 99.999%) flowing at 30 cm³/min for 3 h, flushed overnight at 723 K with Ar flowing at 10 cm³/min, and then cooled to room temperature in flowing Ar. The catalysts were purged overnight in Ar at 723 K to insure that the surface and bulk of the reduced catalyst were free of residual gases. In a few cases we heated the materials in Ar to 723 K after the overnight purge. No residual gases were detected. The materials were dosed by injecting 50 μl pulses of NH₃ (Scott, 99.998%) into the Ar carrier gas stream flowing at 30 cm³/min or exposing the materials to NH₃ flowing at 10 cm³/min for up to 30 min. The materials were then flushed with Ar for 40 min and heated in Ar flowing at 30 cm³/min from room temperature to 723 K at 15 K/min. The catalysts were reduced for at least 3 h and purged overnight between each exposure.

Calibrated pulses of NH₃, N₂, H₂, and O₂ were used to determine response factors for the TCD and mass spectrometer. The relative response factors for the mass spectrometer corresponded closely with those provided by the manufacturer. Response factors for additional gases were calculated based on the manufacturer's correlation. The spectra were normalized by dividing the integrated intensity by the total surface area of material in the reactor. Average peak integration errors were $\pm 20\%$.

RESULTS

Temperature Programmed Reduction

Hydrogen consumption typically started at ~ 550 K; however, the results suggested that reduction of the surface was initiated at much lower temperatures. We will therefore divide our discussion of the TPR spectra according to low ($T_p < 550$ K) and high ($T_p > 550$ K) temperature regions. Results in the low temperature region were similar

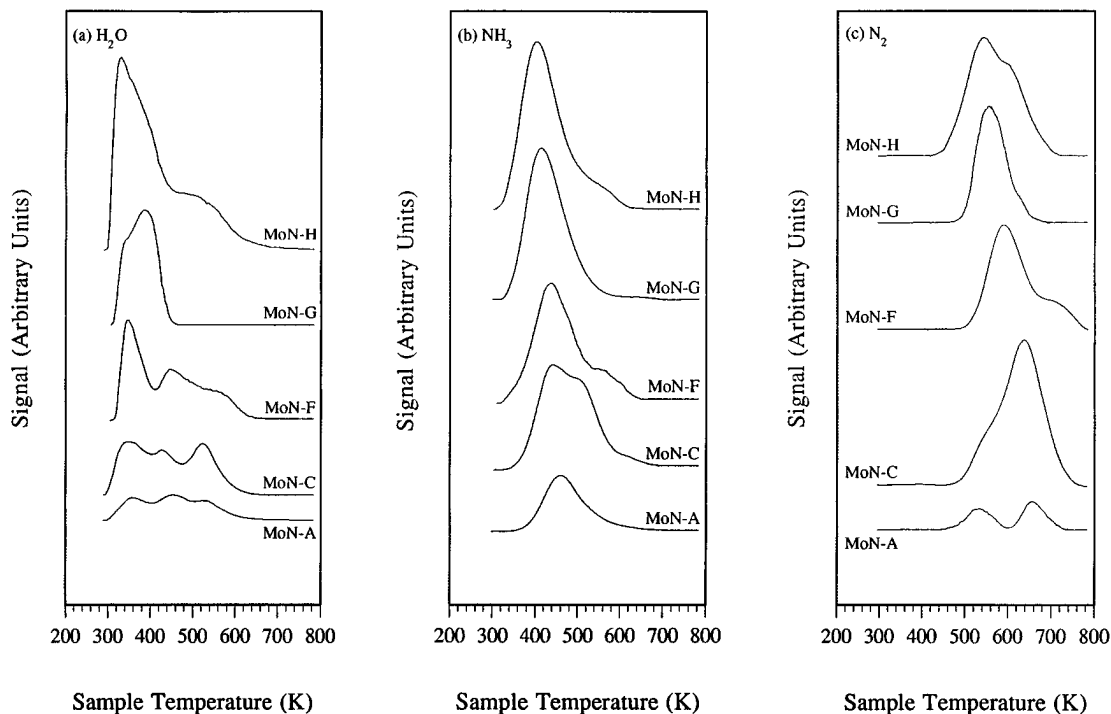


FIG. 1. Desorption of (a) H₂O, (b) NH₃, and (c) N₂ from the passivated Mo nitride surface into Ar as the temperature was increased linearly from room temperature to 773 K.

for desorption into Ar or the H₂/Ar mixture. Species that desorbed into Ar are shown in Fig. 1. We suspect that H₂O that desorbed at temperatures less than ~ 400 K had been physisorbed or weakly chemisorbed. Water that desorbed at temperatures greater than 400 K is believed to be a product of the partial reduction of the passivated surface. Ammonia (Fig. 1b) desorbed from the nitride between 350 and 550 K. This temperature range is similar to that observed during NH₃ TPD suggesting that significant amounts of NH₃ were retained on the surface after synthesis and passivation. The desorption of N₂ commenced at ≈ 450 K (Fig. 1c). Molecular nitrogen usually cannot be removed from γ -Mo₂N at such a low temperature (13, 14), therefore we attributed these peaks to nitrogen evolved during NH₃ decomposition. There was no evidence of concomitant H₂ desorption. Either the hydrogen was retained by the nitride (on the surface and/or in the subsurface), or it was consumed in a subsequent reaction. Under the conditions employed in this study, surface and subsurface hydrogen should desorb from the Mo nitride by ~ 600 K based on our previous H₂ TPD results (3). Therefore we have concluded that the hydrogen liberated during the decomposition of NH₃ reacted with oxygen in the passivation layer to form H₂O. No oxygen containing species (e.g., O₂) other than H₂O were observed.

The amounts of H₂O, NH₃, and N₂ that desorbed into Ar are given in Table 2. Approximately one-third of the total H₂O had been weakly adsorbed and the balance was

produced by the reduction of oxygen in the passivation layer. Using the approximation of 1.1×10^{15} surface Mo atoms/cm² for γ -Mo₂N (15) and assuming an NH₃ to surface Mo atom stoichiometry of unity, the initial coverage by NH₃ residue from the synthesis ranged from 0.18 to 0.75 monolayers (ML). Approximately 20% of the NH₃ residue decomposed.

The consumption of gas phase H₂ and desorption of H₂O and NH₃ were observed in the high temperature region (Fig. 2). Results obtained in this region during H₂ TPR were not observed when the materials were heated in Ar, demonstrating that the desorbed species were reduction products. Ammonia and H₂O desorbed at the same temperature at which H₂ was consumed. This observation suggested that the activation of H₂ was the rate limiting step during high

TABLE 2

Species Desorbed at Temperatures Less Than 550 K during TPR

Sample	H ₂ O (10 ¹⁴ /cm ²)	NH ₃ (10 ¹⁴ /cm ²)	N ₂ (10 ¹⁴ /cm ²)
MoN-A	1.55	2.37	0.16
MoN-C	3.26	5.90	0.36
MoN-F	3.85	6.95	0.54
MoN-G	1.67	1.49	0.26
MoN-H	6.49	6.85	0.72

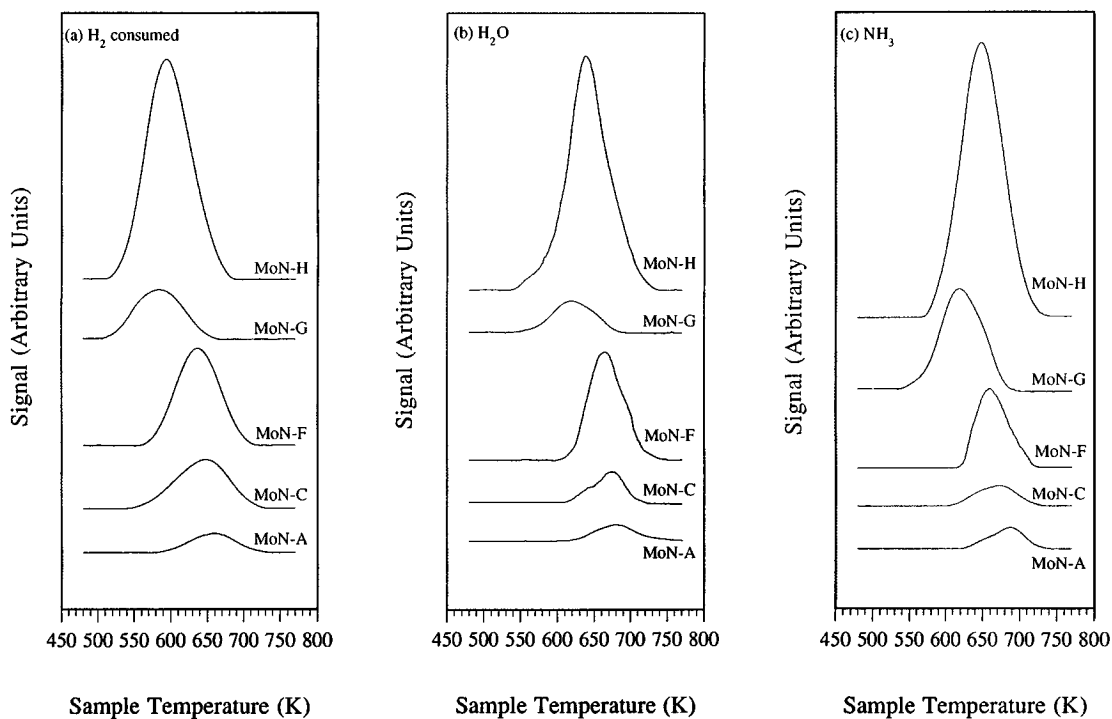


FIG. 2. Consumption of (a) H_2 and desorption of (b) H_2O and (c) NH_3 during H_2 TPR of passivated Mo nitrides.

temperature reduction of and removal of nitrogen from the passivated surface. Since the H_2 consumption peak temperature increased with increasing surface area, we can also conclude that the rate of reduction was controlled by the rate of product nucleation (16, 17).

The quantities of H_2 consumed and H_2O and NH_3 produced during TPR in the high temperature region are given in Table 3. Most of the hydrogen that was consumed was not associated with the production of H_2O or NH_3 . The amount of this excess hydrogen was different for each of the catalysts. Approximately 0.4 ML of excess hydrogen was consumed for MoN-A ($193 \text{ m}^2/\text{g}$); however, the equivalent of nearly 3 ML of excess hydrogen was consumed for MoN-H ($4 \text{ m}^2/\text{g}$), assuming each surface Mo atom represents an adsorption site. Some of the hydrogen may have been retained

on the surface of the nitride (18); however, this cannot reconcile the retention of more than a monolayer of hydrogen. Previously it has been observed that significant amounts of hydrogen can reside on subsurface binding sites in Mo nitrides (3, 19). Therefore we have attributed the retention of hydrogen in excess of a monolayer to the population of subsurface sites. Note that the Mo nitrides that retained the most hydrogen were the most active.

NH_3 Temperature Programmed Desorption

The effects of dose on the NH_3 TPD spectra are shown in Fig. 3 for MoN-E ($28 \text{ m}^2/\text{g}$). Results for the other catalysts were qualitatively similar. Recall that the materials were reduced and degassed prior to the NH_3 TPD experiment. For low coverages all of the adsorbed NH_3 decomposed producing H_2 . The decomposition of NH_3 has previously been reported for γ - Mo_2N powders (11), a $Mo(100)$ - $c(2 \times 2)N$ single crystal (13) and Mo nitride thin films (14). The H_2 desorption peaks shifted to lower temperatures with increasing dose indicating that the rate limiting step was second order (20). Second order reactions that could account for this observation include the recombination of adsorbed atomic hydrogen and the decomposition of adsorbed NH_3 . The temperature at which H_2 desorbed during NH_3 TPD was significantly higher than that during H_2 TPD (3) and since H_2 adsorbs dissociatively at room temperature on Mo nitrides, it has been concluded that the recombinative desorption of atomic hydrogen was not rate limiting. Therefore

TABLE 3

Species Consumed and Produced at Temperatures Greater Than 550 K during TPR

Sample	H_2 consumed ($10^{14}/\text{cm}^2$)	H_2O produced ($10^{14}/\text{cm}^2$)	NH_3 produced ($10^{14}/\text{cm}^2$)
MoN-A	3.10	0.67	0.10
MoN-C	8.34	0.68	0.12
MoN-F	11.5	2.40	0.35
MoN-G	6.87	1.00	0.55
MoN-H	26.2	6.21	1.63

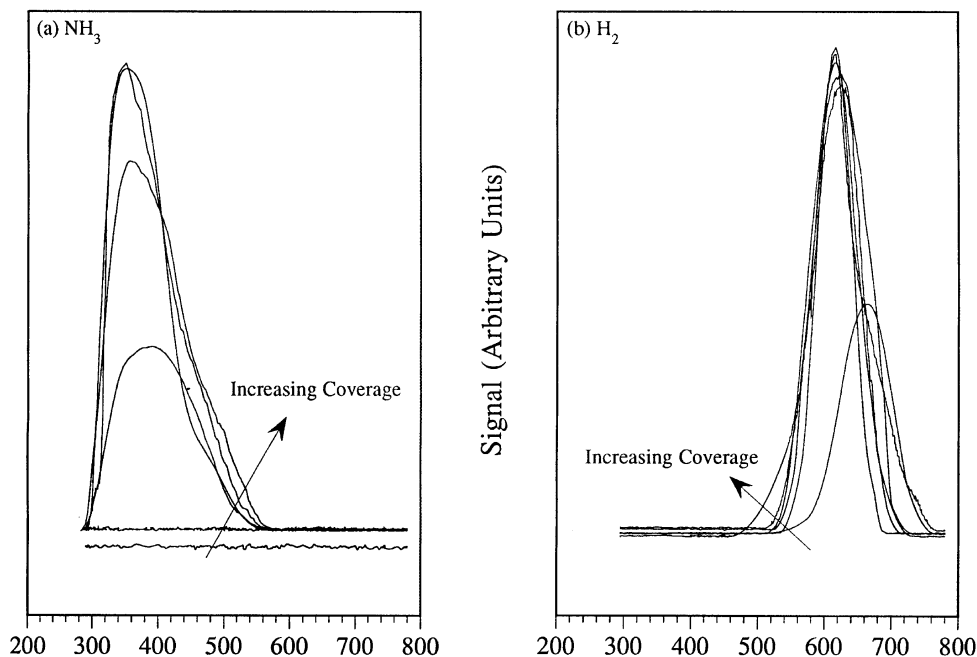


FIG. 3. Desorption of (a) NH₃ and (b) H₂ from reduced MoN-E as a function of NH₃ exposure. Doses ranged from 0.054 to 54 ML. Saturation of the surface corresponded to a dose of ~ 11 ML.

we believe that the decomposition of adsorbed NH₃ was the rate limiting step for H₂ desorption from the Mo nitrides.

At higher NH₃ coverages, NH₃ desorption peaks emerged. The amounts of NH₃ and H₂ that desorbed approached constant values with increasing dose indicating that the adsorption sites were saturated. The uniformity of the surfaces, with respect to the number of types of desorption sites, varied with surface area. The lowest surface area nitrides, MoN-G and MoN-H, possessed two types of NH₃ and H₂ desorption sites while materials with surface areas greater than ~ 20 m²/g possessed single NH₃ and H₂ desorption sites. Most of the NH₃ and H₂ desorbed from the low temperature sites. In general, the low temperature desorption peak for the low surface area materials was coincident with the desorption peak for the high surface area materials. The NH₃ desorption peak temperatures did not shift with increasing dose suggesting that the rate limiting step was first order. For first order desorption, the Redhead equation can be used to estimate the desorption energy (21). Assuming that the pre-exponential factor was between 10^{11} and 10^{15} s⁻¹, the energies required to desorb NH₃ from the Mo nitride surfaces were 24 ± 4 and 32 ± 5 kcal/mol. These values are similar to the energies that we previously determined for the desorption of NH₃ from γ -Mo₂N and β -Mo₁₆N₇ thin films (14).

While the materials differed in their NH₃ adsorption capacities, the desorption sequence was similar. Following saturation of the surface, NH₃ desorbed first as the temperature was increased (Fig. 4a). At higher temperatures, the products of NH₃ decomposition desorbed producing

H₂ (Fig. 4b) and N₂ at temperatures in excess of ≈ 600 K (Fig. 4c).

Table 4 shows the amounts of NH₃ and H₂ that desorbed from the catalysts following saturation with NH₃. We could not quantify the total amount of nitrogen because N₂ continued to desorb up to the maximum operating temperature of the TPD system. Using the amounts of H₂ to determine the amount of NH₃ that decomposed, the initial NH₃ surface coverage ranged from 0.078 to 0.53 ML. However, the ratio of the amount of NH₃ that decomposed to the amount that desorbed molecularly was essentially constant for all the nitrides.

DISCUSSION

Passivation Layer Reduction

The TPR results indicated that passivation incorporated the equivalent to up to one monolayer of oxygen into the Mo nitride surface. This observation is consistent with previous reports that passivation results in the formation of an oxynitride or oxide layer slightly thicker than one monolayer (6, 10, 12). The amount of oxygen removed from the passivation layer (Table 5) was calculated based on the amount of H₂O that desorbed at temperatures in excess of 400 K. Oxygen in the passivation layer on MoN-A (193 m²/g) was equivalent to 0.16 ML, which is similar to the amount reported by Ranhotra *et al.* (22) for a 185 m²/g γ -Mo₂N powder. We note that the most active catalysts had the most oxygen in the passivation layer while the least active materials contained the least amount of oxygen.

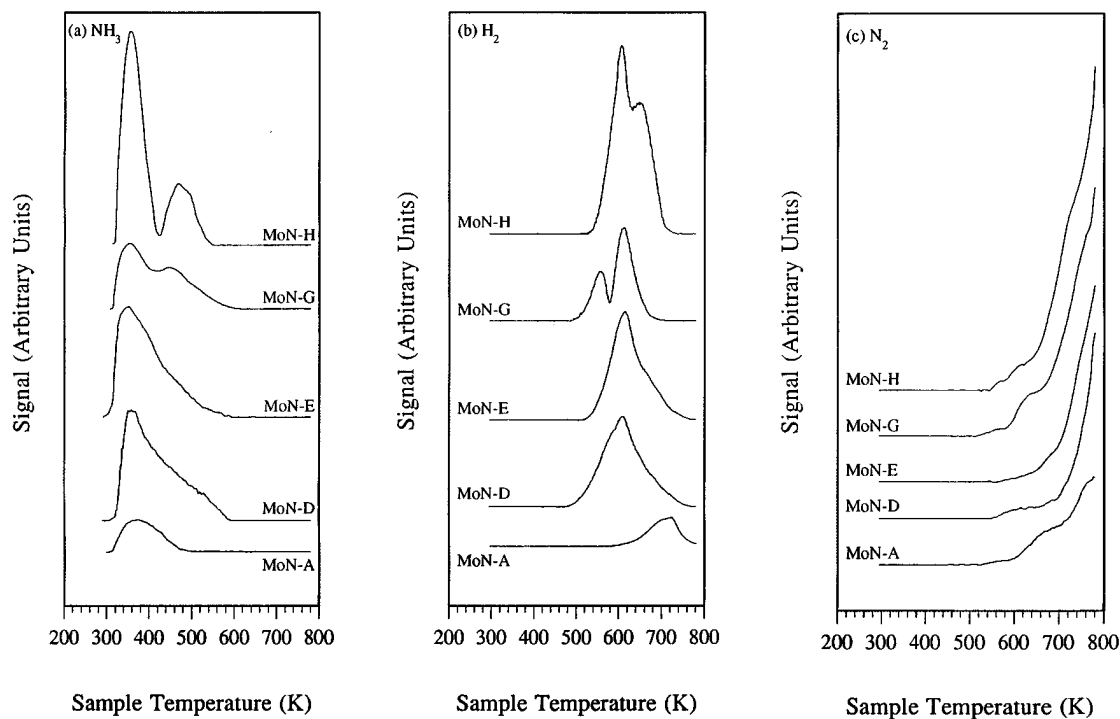


FIG. 4. Desorption of (a) NH_3 , (b) H_2 , and (c) N_2 from the reduced Mo nitrides during NH_3 TPD. Samples were dosed to saturation.

As oxygen is removed from the passivation layer the surface properties of the materials are modified. We found, for example, that the surface areas increased with reduction time and temperature (9). Results presented here suggested that during TPR, oxygen was removed from the surface in two steps: (a) partial removal at temperatures less than ~ 550 K via reaction with hydrogen some of which originated from NH_3 left on the surface after synthesis and (b) complete removal at higher temperatures via reaction with gas phase H_2 . The apparent reduction chemistry is summarized below.

Low temperature reduction:

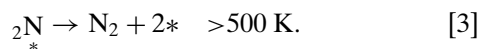
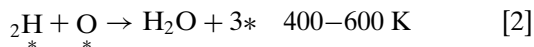
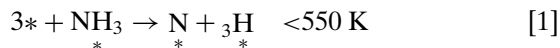
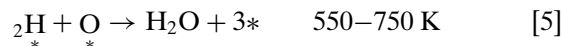


TABLE 4

NH_3 TPD Results Following Saturation of the Mo Nitride Surface

Sample	NH_3 desorbed ($10^{14}/\text{cm}^2$)	H_2 desorbed ($10^{14}/\text{cm}^2$)	NH_3 coverage	
			(ML)	(% Decomposed)
MoN-A	0.62	0.36	0.078	28
MoN-D	2.55	1.42	0.32	28
MoN-E	2.47	1.36	0.31	27
MoN-G	1.70	0.83	0.20	25
MoN-H	4.12	2.57	0.53	29

High temperature reduction:



Ammonia decomposition probably occurred by sequential dehydrogenation as reported by Haddix *et al.* (11) for molybdenum nitride and Oyama (23) for vanadium nitride. The proposed step for NH_3 decomposition over the Mo nitrides is also consistent with reports for other materials (24–26).

TABLE 5

Molybdenum Nitride Reduction Results

Sample	Oxygen in passivation layer ^a (ML)	Percentage of passivation layer oxygen removed via		
		NH_3 decomposition	Hydrogen synthesis residue	Gas phase H_2
MoN-A	0.16	28	33	39
MoN-C	0.25	40	35	25
MoN-F	0.41	36	10	54
MoN-G	0.20	19	35	46
MoN-H	1.0	24	20	56

^a Calculated from H_2O removed via reduction at temperatures in excess of 400 K.

The consumption of hydrogen produced during the decomposition of NH₃ and gas phase H₂ accounted for most of the oxygen removed from the passivated surface. The balance of the oxygen (on average $\approx 25\%$) was removed via an additional reductant, probably hydrogen residue from the synthesis.

By comparing our NH₃ TPD results for the passivated Mo nitrides with those reported for materials that were not exposed to air or O₂, we can assess the influence of passivation on the surface properties of Mo nitrides. Ammonia desorption from the passivated then reduced materials was first order. The first order desorption of NH₃ is inconsistent with the rate limiting step being rehydrogenation of surface NH_x species as has been reported for freshly prepared Mo nitrides (11). The desorption of NH₃ at temperatures lower than that at which NH_x species were reported to form (11) is also inconsistent with the rehydrogenation of NH_x being rate limiting. However, our observation that NH₃ decomposes on the Mo nitrides at temperatures greater than ≈ 500 K is in agreement with reports that the dehydrogenation of NH₃ occurs at temperatures greater than 473 K (11). One would conclude that oxygen introduced during passivation causes a change in the NH₃ desorption mechanism as compared to that for the unpassivated materials but does not alter the NH₃ decomposition mechanism.

Character of Catalytically Active Domains

A number of adsorption methods have been used to characterize the active sites on Mo nitride catalysts (12, 22, 26, 27). We previously used O₂ chemisorption because it has been employed for other types of hydrotreatment catalysts (28). Oxygen chemisorbed uniformly on the Mo nitrides, scaling linearly with the surface area but not with the HDN reaction rate (Table 1). Carbon monoxide behaved in a similar manner with the uptake increasing with surface area (26). The results presented in this paper indicate that NH₃ chemisorption was an effective method for quantifying the active sites. The pyridine HDN reaction rate was proportional to the amount of NH₃ adsorbed (Fig. 5) suggesting that HDN and pyridine adsorption occurred on sites that adsorbed NH₃. Armstrong *et al.* (27) reported that for γ -Mo₂N, NH₃ adsorbed on sites that also adsorbed other organonitrogen compounds including pyridine and acetonitrile. Using linear regression, we determined a turnover frequency, the number of pyridine molecules converted per adsorbed NH₃ molecule per unit time, of $4.1 \times 10^{-4} \text{ s}^{-1}$ ($\pm 0.3 \times 10^{-4} \text{ s}^{-1}$) at 633 K.

The NH₃ TPD results revealed additional characteristics of the catalytically active domains. The fraction of NH₃ that decomposed was coverage dependent. At a sufficiently low coverage, all of the NH₃ decomposed upon heating. As the coverage was increased, NH₃ also desorbed molecularly. The coverage dependence for NH₃ desorption and decomposition, in particular for the higher surface area materials where the saturation coverage was low, implied that NH₃

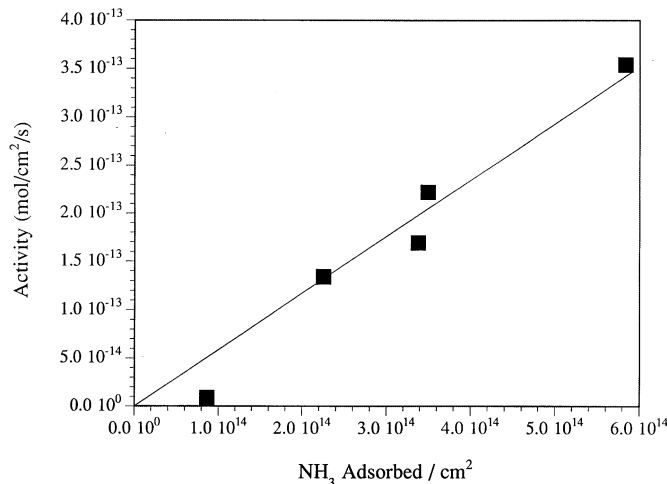


FIG. 5. Mo nitride pyridine HDN activity versus the total amount of NH₃ adsorbed at saturation during NH₃ TPD.

adsorption was localized. At high coverages it is plausible that adsorbed NH₃ formed islands. Ammonia may have adsorbed on nitrogen deficient patches on the Mo nitrides as has been reported for H₂ (18). For the saturated surfaces, approximately three of every four NH₃ desorbed from the surface before the products of NH₃ decomposition were observed, indicating a link between the desorption and decomposition mechanisms. Literature concerning NH₃ decomposition on Mo nitrides helps us reconcile this observation. Ammonia decomposition has been reported to occur via sequential dehydrogenation (11) implying that prior to product desorption, three sites other than the one on which NH₃ is initially adsorbed are required. The NH₃ TPD results also suggested that the interaction of NH₃ with the surface changed discretely with coverage. At low coverages, one would expect NH₃ to interact strongly with the nitride surface favoring decomposition. Strong NH₃–surface interactions present at low coverages may weaken as the coverage increased due to adsorbate–adsorbate interactions. The weakened NH₃–surface bonding would favor molecular desorption of NH₃. Two different types of NH₃ and H₂ desorption sites were identified. For the low surface area, high activity nitrides low and high temperature sites were present while the high surface area, low activity materials possessed only low temperature sites. The lowest surface area materials contained small amounts of Mo metal and the particles were polycrystalline (3, 10), implying that the high temperature NH₃ and H₂ peaks were associated with surface Mo metal (or nitrogen deficient Mo nitride) and/or grain boundaries. Haddix *et al.* (18) suggested that hydrogen adsorbed on nitrogen deficient domains on γ -Mo₂N powders.

CONCLUSIONS

Temperature programmed reduction was used to assess the processes involved in the reduction of passivated Mo

nitrides. The results indicated that the equivalent of up to one monolayer of oxygen was incorporated into the Mo nitrides during passivation. Reduction of the materials in H₂ removed this oxygen as H₂O via reaction with hydrogen from decomposed NH₃ and hydrogen residue from the synthesis at temperatures less than ~550 K, and reaction with gas phase H₂ at higher temperatures. Surface and/or sub-surface nitrogen or NH_x species also reacted with gas phase H₂ at temperatures in excess of ~550 K to produce NH₃.

The pyridine HDN reaction rate increased linearly with the NH₃ adsorption capacity yielding a turnover frequency of $4.1 \times 10^{-3} \text{ s}^{-1}$ at 633 K. This observation also suggested that NH₃ adsorbed on the same sites as pyridine.

While the Mo nitrides differed in their capacities to adsorb NH₃, variations in their NH₃ TPD spectra were qualitatively similar. At low coverages, all of the NH₃ decomposed producing H₂ at 500–700 K and N₂ above 600 K. At saturation, ~75% of the NH₃ desorbed molecularly at 300–500 K and the balance decomposed at higher temperatures. The ratio of molecularly desorbed to decomposed NH₃ was nearly 3:1 for all the materials suggesting that desorption and decomposition occurred on the same sites. We believe that the coverage dependence and link between the desorption and decomposition probabilities at saturation coverage are the consequences of NH₃ adsorption being localized at high coverages. Two different types of NH₃ and H₂ binding sites were observed; low and high temperature sites for the low surface area materials and only low temperature sites for the high surface area materials. The high temperature sites may be associated with the presence of Mo metal and/or grain boundaries in the low surface area materials. Ammonia desorption from the Mo nitrides was first order with energies of 24 ± 4 and 32 ± 5 kcal/mol for the low and high temperature sites, respectively. This suggests that the rehydrogenation of surface NH_x species was not the rate limiting step.

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