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TPD and TPR Studies of Molybdenum Nitride

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The surface species of passivated and nonpassivated molybdenum nitride samples and their stability at elevated temperatures have been investigated by temperature-programmed decomposition and temperature-programmed reduction with H_2. Large differences between fresh and passivated Mo_2N were found. (i) Two types of NH_x adsorbed species remain on the freshly prepared Mo_2N. The first type, weakly adsorbed, desorbed at 200–300°C. Another type is strongly bonded NH_x on the surface of Mo_2N, which decomposed to H_2 and N_2 at 560°C. For passivated Mo_2N samples, only weakly adsorbed NH_x species are present. (ii) An obvious change in the crystalline phase of fresh Mo_2N occurred when it was heated at 850°C in He, while for the passivated Mo_2N sample no change was observed. When Mo_2N was heated to 1000°C, the resulting solid consisted of β-Mo_2N and metallic Mo. Mo_2N is completely reduced to metallic Mo at 880°C in H_2. (iii) The H_2 consumption peak around 470°C for passivated Mo_2N samples is attributed to the reduction of the passivating oxygen. It is suggested that the main effect of passivation on fresh Mo nitride is to eliminate most of the NH_x and H species strongly bonded on nitride and then forming a protective oxide layer. The oxygen incorporated during passivation can be removed by H_2 at a moderate temperature. © 1997 Academic Press

1. INTRODUCTION

Molybdenum nitride as a catalytic material of potential significance has recently received a great deal of attention. It was reported that high surface area molybdenum nitride exhibited outstanding performances for various reactions including NH_3 synthesis (1–3), CO hydrogenation (4), ethane hydrogenolysis (5, 6), quinoline hydrodenitrogenation (7–10), and thiophene hydrodesulfurization (11, 12). While most of the studies focus on the preparation and catalytic activity, little attention has been paid to the influence of passivation treatment upon the surface species existing on molybdenum nitride and its stability at elevated temperature. As fresh molybdenum nitride is very sensitive to oxygen, and rapid autothermal reaction with oxygen leads to serious sintering, in many cases Mo_2N is passivated before use. Therefore, the surfaces of stable molybdenum nitride have been already altered by oxygen during passivation and some changes have occurred.

It was reported that a protective layer of oxide would form on the surface of Mo_2N which has undergone passivation treatment. The amount of oxygen present in passivated Mo_2N was even estimated as large as 19% of the total amount of nitrogen present in pure Mo_2N (11). But the influences on the surface species of Mo_2N caused by passivation are not fully understood. Furthermore, before passivated Mo_2N is employed as a catalyst in catalysts reactions, it is usually activated by H_2 flowing at elevated temperatures, such H_2 reduction at 400°C. It is also not clear whether oxygen incorporated during passivation can be removed by H_2, and what changes of surface species for passivated Mo_2N during treatment in H_2 took place. Therefore, it is useful to study the nature of the surface species formed on molybdenum nitride during its preparation, the changes caused by passivation, and the effect of pretreatment on passivated Mo_2N as well.

The synthesis methodology of molybdenum nitride, using temperature-programmed reaction of MoO_3 with NH_3, reported by Volpe and Boudart (13), has been widely adopted. Temperature-programmed decomposition (TPD) and temperature-programmed surface reaction (TPR) with H_2 are useful techniques for determing the surface species and their reactivity on molybdenum nitride. In this paper, we report the results of TPD and TPR obtained on fresh and passivated molybdenum nitride samples, and discuss the effect of the passivating process on the surface species of molybdenum nitride and the changes in the composition at elevated temperatures with the aid of XRD analysis.

2. EXPERIMENTAL

2.1. *Preparation of Molybdenum Nitride*

Molybdenum nitride was prepared by temperature-programmed reaction of MoO_3 with NH_3. As the nitration of MoO_3 with NH_3 occurs in two steps (14), a two-segment heating program was used to synthesize the molybdenum nitride. After a first quick increase (5°C/min) of the reaction temperature from room temperature to 350°C, the heating rate was controlled at 0.5–1.0°C/min from 350 to 500°C, and 3°C/min from 500 to 700°C. The temperature was kept at 700°C for 2–12 h.

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TABLE 1

BET Surface Area and Average Pore Diameter of Mo_2N

Samples[a]	Heating rate (350–500°C) (°C/min)	NH_3 rate (mol NH_3/mol MoO_3/h)	Surface area (m^2/g)	Average pore diameter (nm)
Mo_2N-A1	1.0	15	22.6	8.9
Mo_2N-A2	0.5	22	76.9	4.9
Mo_2N-A3	0.5	46	103.5	4.8
Mo_2N-B	0.6		133.3	3.8

[a] The symbols A1, A2, and A3 are used to indicate passivated Mo_2N prepared according to the heating rate and NH_3 velocity shown in the table; Mo_2N-B is nonpassivated Mo_2N.

The MoO_3 starting material (Aldrich 99.5%) was pressed into pellets, lightly crushed, and sieved to produce 0.5- to 0.8-mm particles. Then, the MoO_3 particles were charged in a quartz reactor which was placed inside the furnace. The temperature was controlled by a programmable temperature controller and the reaction temperature was measured by a thermocouple which was inside the MoO_3 bed. NH_3 (air liquid 99.95%) was introduced after removing moisture using a moisture filter (Chrompack, gas clean filter) and its flow rate was measured using a bubble flow meter. Molar hourly space velocities of 20–50 mol NH_3/mol MoO_3/h were used. After the reaction was completed, the reactor was quickly cooled to room temperature in flowing NH_3. The nonpassivated sample was directly characterized by TPD and TPR. For passivating samples a He–O_2 (1%) mixture was flowed into the reactor at room temperature overnight.

The molybdenum nitride samples which were used in TPD and TPR measurements are shown in Table 1. Mo_2N-A1, Mo_2N-A2, and Mo_2N-A3 were passivated Mo_2N samples treated by a He–O_2 mixture after the preparation. A1, A2, and A3 represent samples that were prepared by using various heating rates and NH_3 velocities as shown in Table 1. Mo_2N-B was nonpassivated Mo_2N. The BET surface area and pore diameter of Mo_2N were influenced strongly by the synthesis conditions.

2.2. *TPD and TPR Characterization*

A molybdenum nitride sample (0.2 g), charged in the quartz reactor, was heated to 120°C in He and held at this temperature for 1 h. After cooling to room temperature, the sample was heated at 10°C/min to 1030°C in a flow of He (for TPD) or H_2 (for TPR). The flow rate of He and H_2 was 40 ml/min. The effluent steam was monitored for various species as a function of temperature by using an on-line QMS 311 mass spectrometer equipped with a capillary inlet heated by heating tape.

The reductivity behavior of molybdenum nitride was also studied by using a thermal conductivity detector and a mixture of N_2–H_2 (5 v/v%) as reducing gas (TPR-TC). In order to measure H_2 consumption, a cooled trap on *n*-pentane–liquid N_2 (−127°C) was used to remove water formed in the reaction process and NH_3 desorbed from the samples.

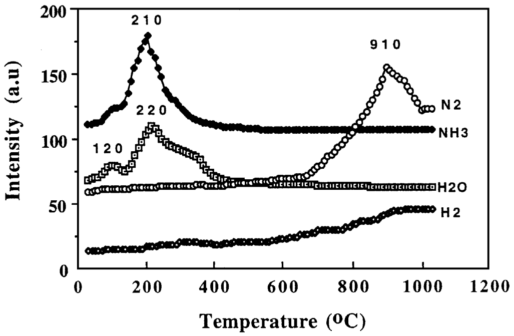

FIG. 1. TPD profile of the Mo_2N-A1 sample (A1 refers to the preparation conditions shown in Table 1).

3. RESULTS

3.1. *TPD of Molybdenum Nitride*

Figures 1–3 show the TPD profiles of passivated molybdenum nitride samples with different surface areas. Four curves of mass/e 2 (H_2), 17 (NH_3), 18 (H_2O), and 28 (N_2) vs temperature of TPD are reported. Obviously, the profiles of various species for Mo_2N-A1, Mo_2N-A2, and Mo_2N-A3 are very similar except for peak intensities. The two peaks of H_2O desorption appear at 120 and 220°C and the NH_3 desorption peak is around 220°C for all these samples. The peak intensities rise with increasing surface area of Mo_2N. On the Mo_2N-A3 sample, a small H_2 desorption peak at about 210°C can be also found, while no H_2 desorption peak appeared on low surface area molybdenum nitride. As for the profile of mass/e 28 (N_2) vs temperature during TPD, the relative intensity of the N_2 signal began to increase gradually when the sample temperature was higher than 600°C. The maximum peak temperature of N_2 desorption is around 910°C. No influence of the surface area of Mo_2N on the N_2 peak temperature is seen, but the peak intensities are much

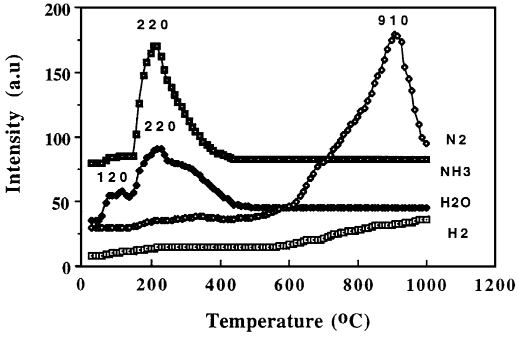

FIG. 2. TPD profile of the Mo_2N-A2 sample (A2 refers to the preparation conditions shown in Table 1).

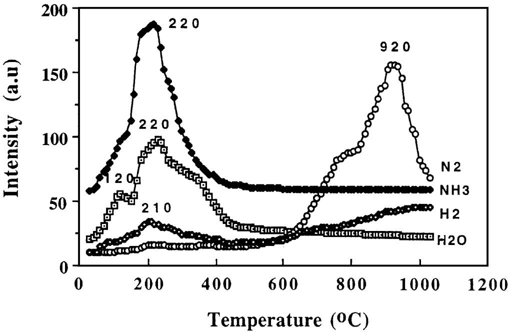

FIG. 3. TPD profile of the Mo_2N-A3 sample (A3 refers to the preparation conditions shown in Table 1).

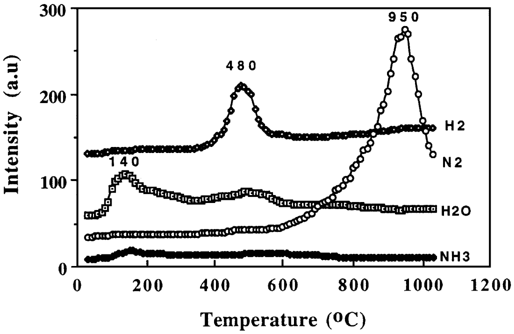

FIG. 5. TPD profile of the Mo_2N-A2 sample following reduction at 400°C in H_2 and flushed at 400°C by He for 2 h.

larger for the Mo_2N-A2 and Mo_2N-A3 samples which have relatively high surface areas. In addition, a small shoulder peak of N_2 at about 700°C can be observed on Mo_2N-A3. The N_2 peak appeared at so high a temperature that it is obviously not the result of the desorption of N_2 adsorbed on molybdenum nitride. We suspect the N_2 peak is from the Mo_2N decomposition at elevated temperatures.

In order to remove surface species, especially to reduce the surface oxygen formed during the passivating process, the passivated Mo_2N-A2 sample was first pretreated at 400°C in H_2 flow at 40 ml/min for 2 h and cooled to room temperature in H_2. The sample was then flushed with He for 4 h and heated in He flow at 40 ml/min from room temperature to 1030°C at 10°C/min. The results are shown in Fig. 4. The NH_3 desorption peak has vanished, but two H_2 desorption peaks appeared at 140 and 480°C. The former is a minor peak which is obviously due to the desorption of some H_2 physically adsorbed or weakly chemoadsorbed on the Mo_2N surface. The latter with a large peak area could reasonably be attributed to the desorption of H_2 strongly bonded to Mo_2N. The complete desorption of this H_2 needs a much higher temperature, and even when the prereduced Mo_2N solid was first flushed with He at 400°C for 2 h, a H_2 desorption peak is also observed during a following TPD process. Of course, the peak intensity is greatly decreased as shown in Fig. 5. It is suggested that the H_2 which desorbed at a high temperature is strongly bonded to the Mo_2N surface or in the crystalline phase of Mo_2N (15).

An obvious influence of the prereduction treatment on the N_2 desorption peak is also seen in Figs. 4 and 5. Comparing these with the Mo_2N sample without H_2 pretreatment, the maximum peak temperature of N_2 over the Mo_2N-prereduced sample shifted from 910 to 950°C. It appears that the removal of surface oxygen on Mo_2N plays a role in inhibiting the decomposition of Mo_2N.

The TPD profile of fresh Mo_2N is shown in Fig. 6. A large difference can be observed as compared with Figs. 1–3. For the nonpassivated Mo_2N sample, the NH_3 desorption peak is broad and around 280°C. A major H_2 desorption peak at 550°C appeared. On the passivated Mo_2N sample the H_2 desorption peak is hardly observed in the TPD process. The N_2 spectra of Mo_2N-B exhibited much larger differences with Mo_2N-A series samples. Three N_2 peaks at 560, 720, and 960°C were observed. N_2 desorption at low temperatures was observed together with the H_2 desorption peak. As Mo_2N-B was not passivated after the preparation in NH_3 flow, it should be suggested that large quantities of NH_3 remain adsorbed on the sample surface. Then, the N_2 peak at 550°C could be considered a result of NH_3 decomposition at an elevated temperature. Two other peaks would be associated with a change of the Mo_2N crystallite itself. The N_2 peak at 960°C is obviously associated with the

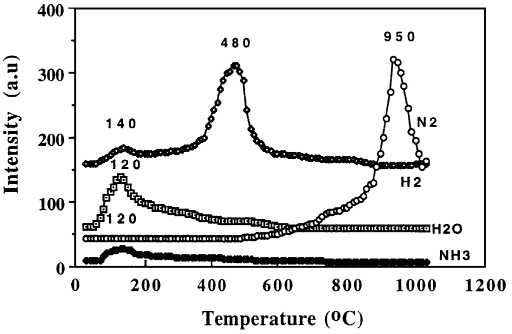

FIG. 4. TPD profile of the Mo_2N-A2 sample prereduced at 400°C in H_2 for 2 h.

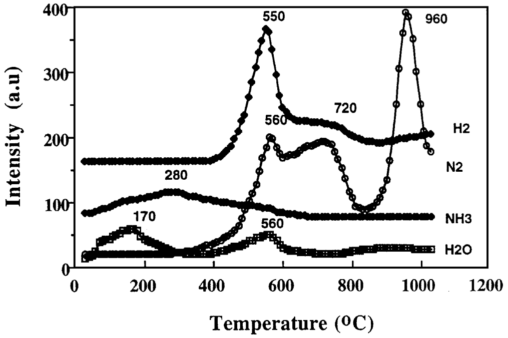

FIG. 6. TPD profile of the Mo_2N-B sample.

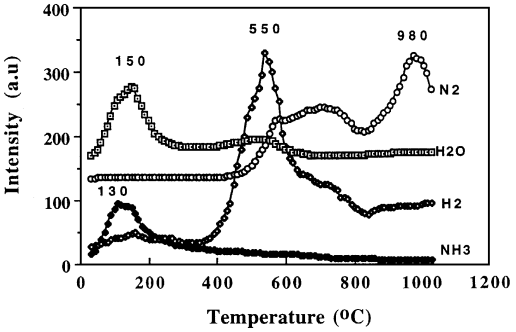

FIG. 7. TPD profiles of the Mo_2N-B sample prereduced at 400°C in H_2 for 2 h.

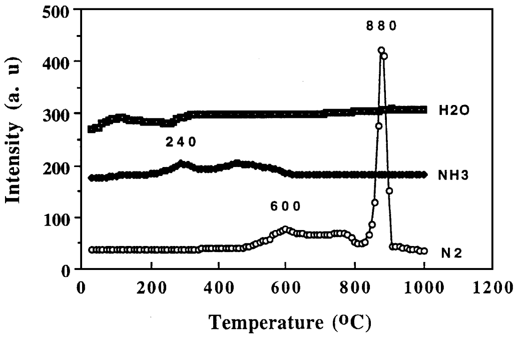

FIG. 9. TPR profile of the Mo_2N-B sample.

decomposition of Mo_2N and is similar to that of the passivated Mo_2N sample. The broad peak of N_2 around 720°C demonstrated that some changes of the Mo_2N crystallite phase occurred.

Figure 7 illustrates the TPD of the nonpassivated Mo_2N sample prereduced at 400°C in H_2. It is seen that a minor NH_3 desorption peak appeared below 200°C, and the H_2 desorption peak around 550°C became much larger as compared with Fig. 6. A large change in the N_2 desorption peaks was also observed. The intensity of the N_2 peak around 570°C decreased obviously. Since this N_2 peak was suggested as due to decomposition of NH_3, a plausible explanation is that most of the NH_3 was desorbed during H_2 prereduction of Mo_2N.

3.2. TPR of Molybdenum Nitride

The TPR-MS profiles for passivated Mo_2N samples are shown in Fig. 8. The change in the H_2 signals was too small to be detected in H_2 flow, and only NH_3, H_2O, and N_2 spectra are observed. It is noticed that the N_2 signal in the temperature region 600–800°C increased slowly, but when the temperature was higher than 800°C, the N_2 signal quickly rose and exhibited a sharp peak at 870°C. This suggests that Mo_2N would be rapidly decomposed in H_2 beyond a definite temperature. Compared to the profile of TPD, the temperature of NH_3 decomposition dropped about 40–50°C. In addition, a broaded NH_3 desorption peak appeared at 220°C.

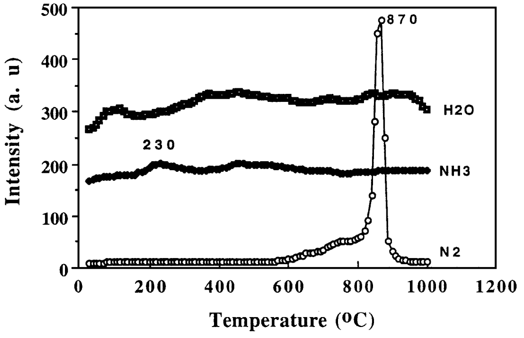

FIG. 8. TPR profile of the Mo_2N-A2 sample.

The TPR-MS profile of the fresh Mo_2N sample as shown in Fig. 9 is similar to that of the passivated Mo_2N sample in Fig. 8. It means that no large difference exist between fresh and passivated Mo_2N samples under H_2 reaction. Of course, for the fresh Mo_2N sample a broad peak in the N_2 signal is more evident in the region 600–800°C. This means there exists the liberation of N_2 in a broad temperature region before the complete decomposition of Mo_2N.

The crystallite changes in the nonpassivated Mo_2N sample after TPD to 850 or 1030°C in He and TPR to 1000°C at 10°C/min were examined by XRD. The results are shown in Fig. 10. For the passivated Mo_2N sample the characteristic

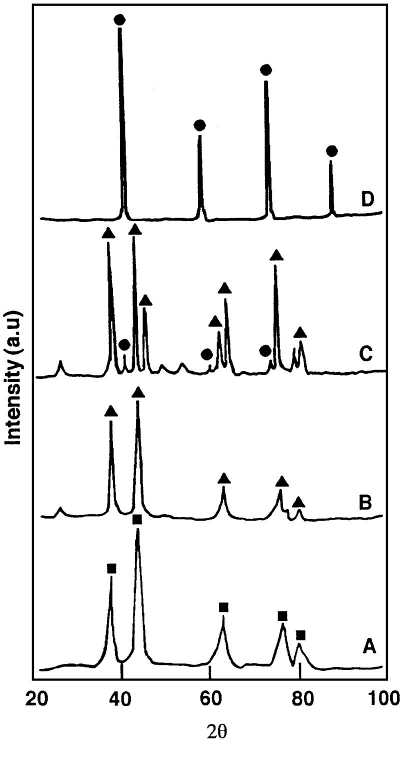

FIG. 10. XRD patters of Mo_2N samples. (A) Passivated Mo_2N; (B) heated to 850°C in He; (C) heated to 1030°C in He; (D) heated to 1000°C in H_2. ■, γ-Mo_2N; ▲, β-Mo_2N; ●, metallic Mo.

bands of γ-Mo_2N are shown in Fig. 10A. When it was heated to 850°C in He, γ-Mo_2N was transformed into β-Mo_2N ($Mo_{16}N_7$). When the temperature was increased to 1030°C, the resulting solid consisted of mixed β-Mo_2N and metallic Mo crystallites. Reduction up to 1000°C reduced Mo_2N completely to metallic Mo. The results demonstrated that the changes in the crystalline phase of Mo_2N would occur before its decomposition at elevated temperatures.

The reaction behavior of the Mo_2N sample with H_2, using a N_2–H_2 (5%) mixture as the reducing gas and a thermal conductivity cell as the detector, was also examined. The TPR-TC profiles of Mo_2N samples are shown in Figs. 11 and 12. In this situation only H_2 signal changes can be observed since all the other gases have been trapped. For the passivated Mo_2N samples with different surface areas, two temperature regions are evident as shown in Fig. 11, i.e., a low-temperature region around 465°C and a high-temperature region around 840°C. Obviously, the peak in the low-temperature region was due to the reduction of surface oxygen on Mo_2N formed during the passivating process. The peak in the high-temperature region is attributed to the results of the liberation of N_2 due to Mo_2N decomposition. For the nonpassivated Mo_2N sample, three temperature regions are observed: (i) two H_2 consumption peaks around 300 and 500°C appeared, (ii) a minor H_2 evolution peak is seen in the region 550–700°C, and (iii) a major N_2 liberation peak appeared around 840°C, which is the same as observed on the passivated Mo_2N sample. The appearance of the H_2 consumption peak in the low-temperature region revealed that some H_2 consuming species are present on the nonpassivated Mo_2N sample. It is suggested that the desorption of NH_x species ($x = 1$–3) adsorbed on the Mo_2N surface and the reduction of a residual trace of oxide during MoO_3 nitridation are probably responsible for the H_2 consumption. The broad H_2 evolution peak is due to either the desorption of H_2 adsorbed on the Mo_2N sample or the release of H_2 upon NH_3 decomposition, which is observed only on the nonpassivated Mo_2N sample. This is consistent with the TPD-MS data.

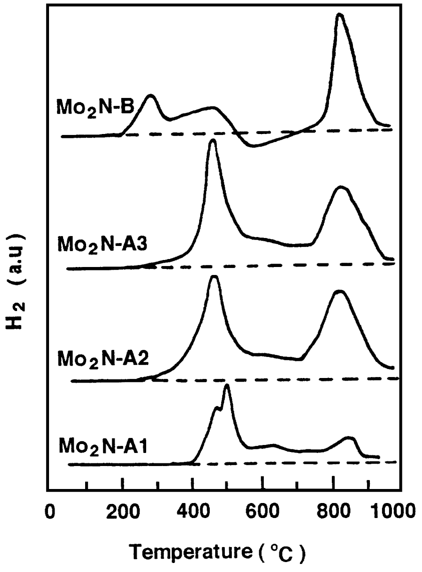

FIG. 11. TPR-TC profile of passivated Mo_2N (A1, A2, A3) and fresh Mo_2N (B).

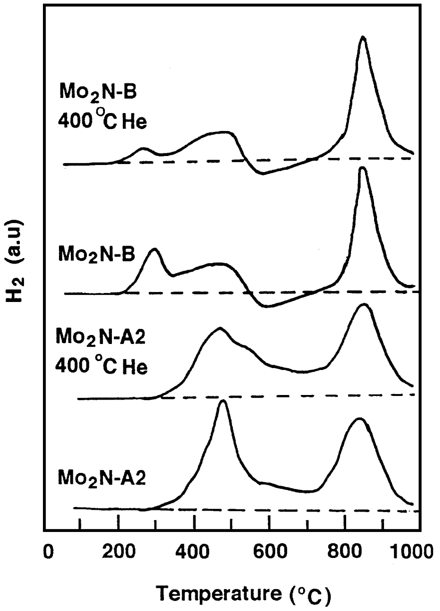

FIG. 12. The influences of pretreatment at 400°C in He on TPR-TC profiles of Mo_2N.

Figure 12 presents the results of first pretreating the Mo_2N sample at 400°C in He flow for 2 h, and then examining it by TPR-TC. For the passivated Mo_2N sample, the H_2 consumption peak of the low-temperature region became slightly broaded, while for the nonpassivated Mo_2N sample, the intensity of the H_2 peak at 300°C decreased greatly.

4. DISCUSSION

4.1. *Surface Species on Molybdenum Nitride*

Due to the high surface area of Mo_2N and the method of preparation by reaction of MoO_3 and NH_3, it is reasonable to consider that ammonia adsorbed on the Mo_2N surface. It was reported that a considerable amount of NH_3 is desorbed from passivated Mo_2N samples in the temperature region 200–300°C (16). Nagai *et al.* also observed the presence of NH_3 desorption peaks on nitrided molybdena-alumina (12). Haddix *et al.* suggested that ammonia can be held in several states, such as NH_3, NH_2, and NH, on the Mo_2N surface (15). Thus, it is suggested that NH_x species always remain on the Mo_2N surface. From our results, the differences in NH_x species adsorbed on the passivated Mo_2N and on the nonpassivated Mo_2N samples are evident. For Mo_2N-passivated samples, only a NH_3 desorption peak around 220°C was observed as shown in Figs. 1–3. When the temperature was beyond 400°C, the NH_3 desorption curve became a horizontal line. However, for the nonpassivated Mo_2N sample, the ammonia desorption peak is very broad (from 100 to 600°C). We suspect that another NH_x species, which would decompose to N_2 and H_2 at elevated temperatures, exists. In Fig. 6, the N_2 and H_2 desorption peaks around 560°C actually come from the decomposition of NH_x adsorbed on the sample surface. Therefore, it is suggested that two kinds of NH_x species remain on the nonpassivated Mo_2N surface. The first kind, desorbed below 300°C, is weakly chemisorbed. Another kind, strongly chemisorbed on the surface, was formed during the synthesis of Mo_2N at 700°C under NH_3. For the passivated Mo_2N, only a weakly adsorbed ammonia species is present on the surface.

Studies have shown that molybdenum nitride exhibits significant capacities for adsorbing hydrogen (17). It was suggested that irreversibly held H_2, strongly bonded to the nitride surface, may occur on nitrogen-deficient patches of Mo present on the nitride surface. For the passivated Mo_2N sample a small peak of weakly adsorbed H_2 was observed only on the high surface area sample. It means that no significant amount of H_2 remained on the passivated Mo_2N. When this Mo_2N sample was reduced in H_2 at 400°C, two H_2 desorption peaks were evident (Fig. 4). The minor H_2 peak desorbed at a low temperature could be considered as adsorbed on the surface of Mo nitride, while H_2 desorbed at a high temperature could probably be attributed to unsaturated coordinative sites on the surface, or in the subsurface sides or bulk of Mo_2N. The second type of hydrogen can be retained up to 480°C. In TPD profiles of freshly prepared Mo_2N, except for H_2 release around 550°C, there is no other H_2 desorption peak. We suspect that, as the freshly prepared Mo_2N was cooled to room temperature in NH_3 flow, most of the H_2 formed during the synthesis of Mo_2N at high temperatures could be flushed out by NH_3 in the decreasing temperature process. Another reason is that a part of H_2 adsorbed on Mo_2N could react with NH_2 or NH species existing on the Mo_2N surface forming NH_3. Comparing Figs. 6 and 7, it is seen that when the fresh Mo_2N was reduced in H_2 at 400°C, the area of the H_2 desorption peak around 550°C is much larger. The increase of H_2 is attributed to the desorption of H_2 remaining on Mo_2N during reduction.

In conclusion, there are two types of NH_x adsorbed species that are weakly adsorbed and strongly bonded on the fresh Mo_2N surface. The latter can be decomposed to N_2 and H_2 around 560°C. A kind of H species probably occupies nitrogen-deficient patches of Mo on the surface or enter into the lattice of nitride. The passivated Mo_2N solid has only a weakly adsorbed NH_x species, which would desorbed below 300°C.

4.2. The Influence of Passivation Treatment on Mo_2N

Some unsaturated coordinative sites remain on the fresh Mo nitride surface. The NH_x or H species formed during NH_3 decomposition at elevated temperatures could be strongly adsorbed on these sites. A considerable amount of active H atoms can also enter into the lattice of Mo nitride (17). A rapid autothermal oxidation of adsorbed NH_x species and hydrogen species would result upon exposure to air.

Furthermore, oxygen incorporated during passivation forms a protective layer on the surface. It has been suggested that (14, 15, 18, 19) passivated oxygen is chemisorbed on the nitride surface, and one or two monolayers of oxide are formed, or oxygen diffuses into the lattice forming an oxynitride. Our TPR-TC data indicated that the reduction peak of the oxide forming the passivation layer appeared around 470°C, which is almost the same as the reduction temperature of the M=O bond in MoO_3 (20). This suggests that the oxygen was bonded to Mo atoms on top sites, which was considered to be where NH_x was bonded originally (15). Of course, it is not excluded that a part of the surface layer oxygen diffuses into the subsurface of Mo nitride, since the TPR reduction peak is very wide.

The reduction treatment on Mo_2N samples at elevated temperature removed the surface layer oxygen formed during passivation. It was observed in Fig. 4 that the H_2O peak at 220°C was eliminated by oxygen removal. But the surface properties are modified after the removal of oxygen. The release of the N_2 peak was delayed to 950°C, and a large H_2 desorption peak appeared at 480°C. As for fresh Mo_2N reduced in H_2 at 400°C, the H_2 desorption peak around 550°C became much larger, indicating that a large amount of hydrogen is retained in Mo_2N.

We suspect that the main effect of passivation on freshly prepared Mo_2N is to eliminate most of the NH_x and H species strongly adsorbed on the unsaturated coordinative sites of nitride and to form a protective oxide layer. This oxygen can be reduced by hydrogen at elevated temperature, but the surface state of Mo_2N reduced in H_2 at elevated temperatures is modified by the reduction.

5. CONCLUSION

The surface of fresh Mo nitride prepared by the temperature-programmed reaction of MoO_3 with NH_3 retains significant amounts of NH_x and H species formed during NH_3 decomposition at elevated temperatures. The part that is weakly chemisorbed NH_x species can be desorbed at temperatures lower than 300°C, while that part bonded strongly to Mo atoms is decomposed and forms H_2 and N_2 at temperatures over 550°C. When Mo nitride was passivated in a $He-O_2$ (1%) mixture, only a small amount of weakly adsorbed NH_x was retained. The oxygen would be bonded to Mo atoms to occupy the original positions of NH_x species and formed a protective layer. Part of the oxygen can diffuse into the subsurface of Mo_2N, but no separated MoO_3 phase appeared. A major reduction peak of passivated Mo nitride was observed at 470°C. It means that the oxygen incorporated during passivation can be removed by H_2 at moderate temperatures. The surface of reduced Mo_2N is modified by the reduction in H_2.

When fresh Mo_2N was heated in He over 1000°C, it would transform first from γ-Mo_2N to β-Mo_2N, and then gradually decompose to metallic Mo. For passivated Mo_2N no obvious changes in the crystalline phase occur before its decomposition. Mo_2N can be completely reduced to metallic Mo by hydrogen below 1000°C.

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