

Temperature-Programmed Desorption of CO and NO over γ -Mo₂N

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The temperature-programmed desorption–mass spectroscopy technique has been used to characterize the desorption behaviors of adsorbed CO and NO on γ -Mo₂N. It has been found that adsorbed CO is desorbed with a prominent peak at 383 K and a shoulder at 423 K, without evidence of any decomposition. This suggests that the aggressive adsorption of molybdenum toward CO has been modified considerably by nitridation to resemble the properties of the Group VIII metals. After synthesis there is some NH₃ left on the Mo₂N sample, which decomposes upon heating and the hydrogen liberated helps reduce the sample to certain extents, according to the conditions employed. Reducing the sample with hydrogen at high temperatures can produce coordinatively unsaturated sites of Mo whose number and nature are important to the interaction between the sample and CO and NO. Three types of active sites on the reduced Mo₂N to adsorb NO with low, medium, and high adsorption energies have been found, from which NO is desorbed at 393, 503, and 543 K, respectively. In addition to NO, N₂ and N₂O were detected as desorption products, which suggests that adsorbed NO undergoes decomposition and disproportionation reactions under appropriate conditions. The results of NO adsorbed on H₂-preadsorbed Mo₂N show that the adsorption and reaction of NO on the sample is very much affected by preadsorbed hydrogen dosed at 673 K. The reactions between the reversely migrated hydrogen and the other surface species have also been discussed. © 1998

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1. INTRODUCTION

Since Volpe and Boudart (1) reported that high-surface-area γ -Mo₂N can be prepared by reducing MoO₃ with NH₃ in a temperature-programmed manner, γ -Mo₂N has been of wide interest in heterogeneous catalysis. A significant number of works have been reported on its synthesis (2–5), catalytic properties (6–12), and characterization (13–21). It has been found that γ -Mo₂N exhibits outstanding performance in a series of hydrogen-involved reactions including NH₃ synthesis (6), ethane hydrogenolysis (7), CO hydrogenation (7, 8), and hydrotreating (HDN, HDS) (8–12).

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It is important to gain a deeper insight into the nature of the surface active sites of γ -Mo₂N in order to understand its excellent catalytic performance. Unfortunately, it is difficult to study its surface properties by using optical spectroscopy, as γ -Mo₂N is opaque in the infrared region. The NMR technique has been used to study the adsorption of unsupported γ -Mo₂N by Bell, Reimer, and co-workers (13–17). The desorption behaviors of H₂ (18, 19), NH₃ (15, 20, 21) and pyridine (17) adsorbed on γ -Mo₂N have been studied by several groups. However, to our knowledge no results of NO adsorption/desorption on γ -Mo₂N have been reported so far. It is of importance to study the adsorption/desorption behaviors of both CO and NO on γ -Mo₂N, as the sites to adsorb CO and NO are believed to be related to the active sites in hydrotreating and some hydrogenation reactions (22–24). Furthermore both CO and NO are important contaminants released from thermal engines, especially through automobile exhaust, whose adsorption and reactions on γ -Mo₂N will be of interest from the view of environmental protection.

In this paper, we are reporting the temperature-programmed desorption–mass spectroscopy (TPD-MS) results after ¹³CO and NO adsorption on γ -Mo₂N. It has been found that there are two types of active sites to adsorb CO and three types of sites to adsorb NO. The majority of adsorbed CO is desorbed molecularly with a small portion undergoing disproportionation. On the other hand there are both molecular and dissociative adsorptions of NO, and N₂O is also observed at high temperatures, supposedly to be the product of a NO disproportionation.

2. EXPERIMENTAL

The Mo₂N sample used in this study was synthesized by temperature-programmed reaction (TPR) of MoO₃ with ammonia as described elsewhere (1, 5). Briefly MoO₃ was uniformly heated in flowing ammonia from room temperature to 573 K at a heating rate of 10 K/min, and from 573 to 973 K at 1 K/min. Then the sample was kept at 973 K for 2 h to completely transform MoO₃ to molybdenum nitride. After synthesis, the sample was cooled to room temperature in flowing ammonia and passivated in a stream of 1% O₂/N₂

to avoid violent oxidation when exposed to air. This sample is called passivated Mo₂N. XRD proved that the passivated sample was bulk γ -Mo₂N. The BET surface area of the sample was 82 m² g⁻¹. XPS experiments were carried out using an SSX-100 Type 206 (Surface Science Instruments) spectrometer with an aluminum anode at 10 kV and 15 mA.

The temperature-programmed desorption experiments were carried out in a homemade glass apparatus, where samples can be heated, evacuated, oxidized, and reduced and gasses can be dosed for adsorption. The reactor used in this study was a U-shaped quartz tube with a quartz frit on the bottom to hold the sample. Passivated samples were pretreated in three different ways: (1) after being evacuated at 773 K for 1 h and cooled to room temperature under vacuum it is called evacuated Mo₂N; (2) after being reduced in flowing H₂ with a flow rate of 60 ml/min at 673 K for 2 h and evacuated at 773 K for 1 h, the sample was cooled to room temperature under vacuum, and it is called reduced Mo₂N; (3) after being reduced in flowing H₂ with a flow rate of 60 ml/min at 673 K for 2 h and cooled to room temperature in hydrogen, the sample was evacuated, and it is called H₂-preadsorbed Mo₂N. A separate TPD run was carried out to confirm that there was no hydrogen left on the reduced Mo₂N. A typical TPD experiment was performed as follows: a 50-mg sample was put into the reactor and treated under various conditions as required. Then it was exposed to 30 Torr (1 Torr = 133.3 N m⁻²) ¹³CO or NO for 30 min to ensure a saturated adsorption. Subsequently, the system was evacuated and the sample was heated with a heating rate of 10 K min⁻¹ from room temperature to 773 K or higher. During TPD a small part of the desorption products was introduced into the chamber where the mass spectrometer was housed, through a leak valve and the gas phase composition was analyzed using a 16-channel SX 200 Mass Spectrometer (VG Gas Analysis, Ltd.). The signals of $m/e = 2, 12, 13, 14, 16, 17, 18, 28, 29, 30, 32, 44,$ and 45 were monitored simultaneously and recorded by a PC.

3. RESULTS AND DISCUSSION

3.1. Composition of the Catalysts

In Table 1 the XPS results of the nitride sample used before and after reduction at 673 K are tabulated. Obviously the sample was covered by oxygen introduced during passivation before reduction. After reduction the amount of oxygen decreased, but not completely; therefore the sample used was actually a kind of oxy-nitride. This is consistent with the literature (18, 25). On the other hand the oxidation states of the Mo species decreased after reduction, as displayed in the last column, which shows more Mo in lower oxidation state.

TABLE 1
XPS Results of the γ -Mo₂N Sample before and after Reduction at 673 K

	Atomic ratios		Binding energy (eV)		Binding energy of Mo 3d _{5/2} at various states and the percentages of the Mo species		
	N/Mo	O/Mo	N(1s)	O(1s)	Mo ⁶⁺	Mo ⁴⁺	Mo ⁵⁺
Before	2.4	1.9	397.2	530.2	232.5(39)	230.0(19)	228.8(42)
After	0.49	0.57	397.2	530.2	232.5(11)	230.2(28)	229.0(61)

3.2. ¹³CO on Reduced Mo₂N

Figure 1 shows the TPD results from a ¹³CO adsorbed reduced γ -Mo₂N. The ¹³CO ($m/e = 29$) curve shows a desorption peak at 383 K and a shoulder at 423 K, suggesting two types of active sites for the molecular adsorption of CO. In addition a small desorption feature of ¹³CO₂ ($m/e = 45$) at 423 K is detected, which may be attributed to a product of CO oxidation with surface oxygen, or one from CO disproportionation. From the coincident ¹³CO₂ and ¹³CO desorptions, we prefer the postulation of CO disproportionation. We suggest that CO is adsorbed molecularly at two types of sites on the γ -Mo₂N, and a smaller number of sites have higher adsorption energy. Upon heating the sample to around 420 K, the majority portion of CO adsorbed there is desorbed, while the other portion undergoes disproportionation to release CO₂, leaving oxygen species on the sample.

Haddix *et al.* (14) reported the results of a ¹³CO NMR study of CO adsorbed on Mo₂N. They concluded that CO bonds in a molecular state on γ -Mo₂N. Also they inferred, from the same chemisorption capacity of γ -Mo₂N for NH₃ and CO, that CO bonds to Mo in an on-top mode (26). From our TPD results CO also adsorbs molecularly, and we think that the small number of CO adsorption sites with higher adsorption energy, which Haddix *et al.* (14) did not observe, may be caused by the differences in preparations. The above results are rather interesting as on pure molybdenum CO is very easy to decompose, leaving atomic carbon and oxygen on the surface (27, 28). By nitridation the aggressive adsorption of molybdenum toward CO is successfully modified to a much milder manner to resemble the properties of the Group VIII metals. This is certainly one of the requirements the nitrides must meet before they can be a good replacement for the rare and expensive noble metals. Very recently we observed, using FTIR, two intense CO vibrations at 2200 and 2045 cm⁻¹ after *in situ* renitriding a passivated Mo₂N/Al₂O₃ sample and subsequent CO dosing, which are assigned as CO adsorbed on N and Mo sites, respectively (29). The present report is again a piece of evidence in favor of the prediction that nitrides and carbides

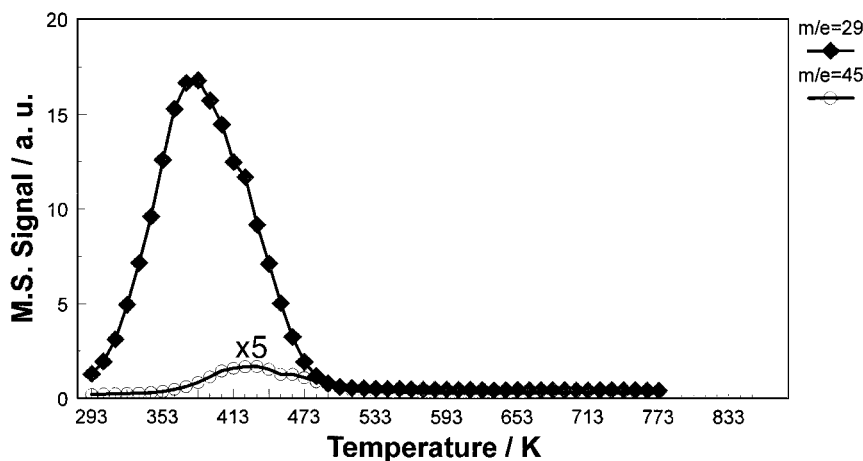


FIG. 1. TPD profiles of ^{13}CO adsorbed on reduced Mo_2N .

are promising in replacing the Group VIII metals in some applications in catalysis.

3.3. TPD of Passivated Mo_2N without Dosing Anything

The passivated sample was evacuated for 1 h at room temperature before the TPD run was performed, without dosing anything. As shown in Fig. 2, NH_3 ($m/e=17$) desorption starts at a temperature as low as 343 K and reaches a maximum at 523 K. H_2O desorption ($m/e=18$) shows two peaks at 383 and 553 K. We suggest that the H_2O desorbed around 383 K is chemisorbed H_2O (25), while that at 553 K is associated with NH_3 . It is supposed that a part of the ammonia retained after preparation dissociates into atomic hydrogen and nitrogen. The former is active to react with surface oxygen introduced during passivation to form water, while the latter recombines to form molecular nitrogen. At the same temperature a nitrogen peak ($m/e=28$) is discerned, which supports our suggestion. Another $m/e=28$ desorption peak

is observed at 803 K, which seems to be from the recombination of lattice nitrogen (20, 30). An $m/e=14$ curve (not shown) resembling that of $m/e=28$ excludes the possibility that the mass 28 features are from randomly adsorbed CO. No hydrogen desorption has been observed, which is consistent with the literature (31).

The results strongly suggest that NH_3 remains on Mo_2N samples at the end of synthesis. Upon heating a passivated sample, hydrogen produced from the decomposition of the ammonia can reduce the sample to a certain extent, as proved by the formation of H_2O and N_2 . Colling *et al.* (21) reported that approximately 20% of the NH_3 residue decomposed upon heating. Haddix *et al.* (15) pointed out that ammonia was adsorbed molecularly on $\gamma\text{-Mo}_2\text{N}$ at room temperature and the adsorbed NH_3 underwent progressive dehydrogenation to produce NH_2 and NH groups as well as N and H atoms upon heating under vacuum. Our results reveal that the hydrogen thus produced is highly active and can easily react with the oxygen species on the passivated

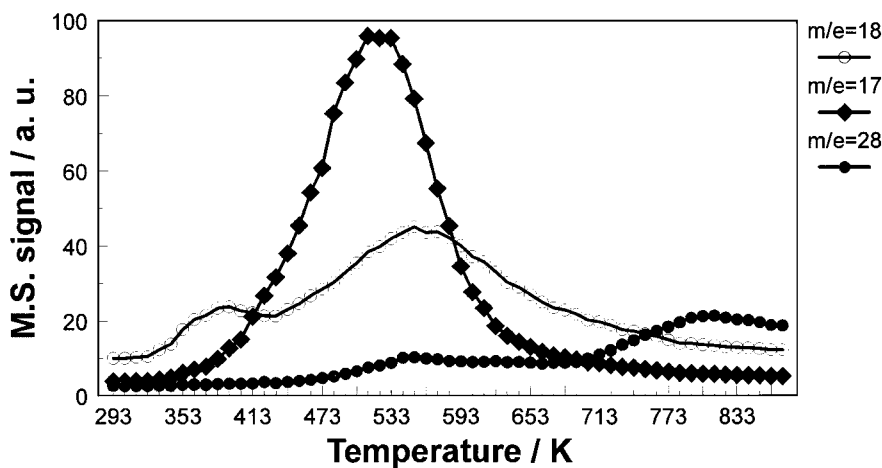


FIG. 2. TPD profiles of passivated Mo_2N evacuated at room temperature, without any adsorption.

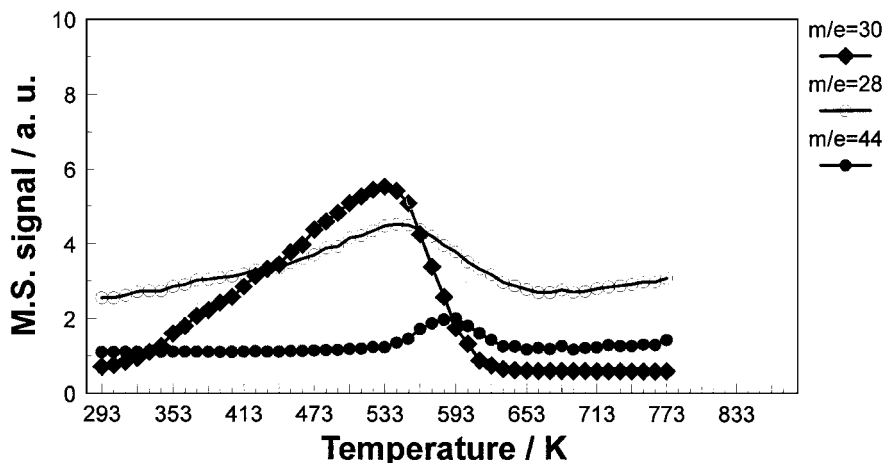


FIG. 3. TPD profiles of NO adsorbed on evacuated Mo₂N.

layer. Consequently, by evacuating the passivated sample at high temperatures, some coordinatively unsaturated Mo sites (CUS) with oxygen and/or nitrogen deficiency could be produced (13).

3.4. NO on Evacuated Mo₂N

Figure 3 shows the TPD profiles after NO was adsorbed on evacuated Mo₂N. It can be found that NO ($m/e=30$) desorption starts almost immediately when the sample is heated and reaches a maximum at 533 K. The N₂ ($m/e=28$) desorption shows a broad peak from around 300 K, with a maximum at 543 K. From 538 K another species, N₂O ($m/e=44$), is detected which peaks at 593 K. It is quite clear from the aforementioned results that there are both molecular and dissociative adsorption of NO on the evacuated Mo₂N. Many authors believed that molecular NO is adsorbed on Mo-containing catalysts such as sulfided Mo/Al₂O₃ in dinitrosyl or dimer (24). At this point we do

not know exactly when NO decomposition takes place, on the basis of our results. However, it has been proposed from the literature (32) that NO adsorbs on transition metals dissociatively at first and molecular adsorption takes place later.

A few lines should be given to the origin of N₂O. There are two possible routes for its formation. One is a direct nitridation to the molecularly adsorbed NO, with surface N. The other is the disproportionation of NO. We shall discuss this topic further in later parts.

3.5. NO on Reduced Mo₂N

The TPD results after NO adsorbed on reduced Mo₂N are shown in Fig. 4. NO, N₂, and N₂O are desorbed in amounts larger than those shown in Fig. 3 but with similar shapes. NO is desorbed at 543 K, a much higher temperature than for CO desorption. Furthermore, two shoulders at 393 and 503 K can be seen with NO desorption ($m/e=30$). The N₂

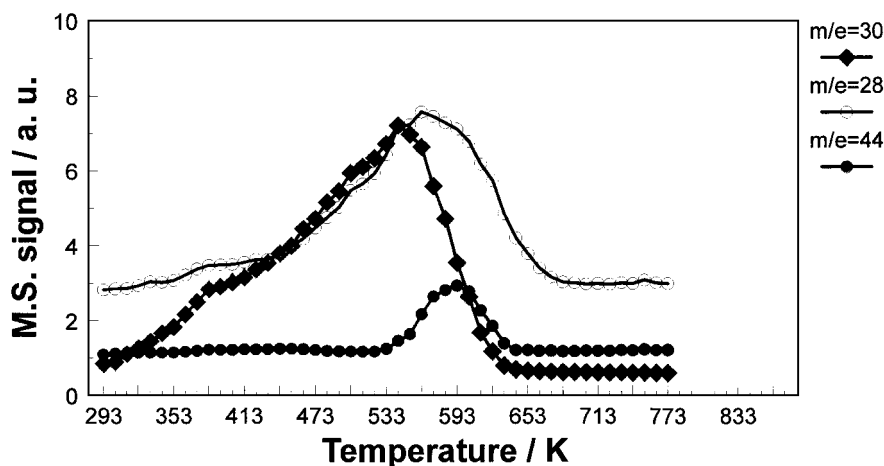


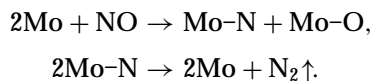
FIG. 4. TPD profiles of NO adsorbed on reduced Mo₂N.

desorption maximum is at 563 K, also with two shoulders at 393 and 503 K, the same as those of NO shoulders. N₂O ($m/e=44$) desorption peaks at 593 K, which coincides with the N₂O desorption from the evacuated sample.

Obvious similarity exists between the desorptions from the evacuated and the reduced samples (Figs. 3 and 4). However, three differences can be distinguished: (1) The desorbed species from the reduced sample are of amounts larger than those from the evacuated sample, indicating higher adsorption ability of the former, and hence larger population of the active sites on the sample surface. (2) The desorbed NO and N₂ from the reduced sample are released at slightly higher temperatures, indicating a stronger adsorption on the reduced sample than on the evacuated one. (3) The shoulders of the NO and N₂ desorptions from the reduced sample are better resolved. The passivated sample is covered with a thin layer of oxygen; the only means to remove this is the hydrogen from the residual NH₃ during a brief heating, which is certainly a poor way to activate the sample. With the evacuated sample the Mo₂N is heated during evacuation, which gives the surface NH₃ a better chance to decompose and the formed hydrogen to react with the oxygen layer and perhaps the lattice N as well, so that the active sites on the surface are formed with a population larger than that in the case of the passivated sample. When the Mo₂N sample is reduced in flowing hydrogen, not only is the residual NH₃ allowed to react at elevated temperature, but extra hydrogen is supplied as well, which should be able to form more active sites on the surface, perhaps coordinatively unsaturated ones with oxygen and/or nitrogen deficiency (CUS).

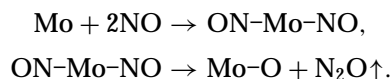
It is worth noting that the property of Mo₂N in NO adsorption is very similar to that of Group VIII metals. It has been discovered that NO can be both molecularly and dissociatively adsorbed on the Group VIII metals (33, 34), and that N₂ is evolved during desorption. Also studies of NO adsorption on reduced MoO₃/Al₂O₃ catalyst gave evidence that NO was adsorbed on the Mo atom in a dimer or dinitrosyl state (24, 35). Our IR results of NO adsorbed on molybdenum nitrides supported on silica and alumina also show that NO can be adsorbed on the samples in a dimer or a dinitrosyl form (36). Therefore the following mechanism for NO adsorption on reduced γ -Mo₂N surface is suggested:

(1) NO can be dissociatively adsorbed on reduced γ -Mo₂N surface, and N₂ evolves during desorption:

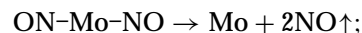


(2) At other active sites, perhaps the CUS, NO can be adsorbed in a dimer or a dinitrosyl form, and N₂O evolves during desorption as a result of a disproportionation of the

dimer or dinitrosyl NO, leaving an oxygen atom on Mo:



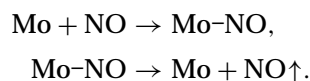
Molecularly desorbed NO may also come from the dimer or dinitrosyl adsorption:



and N₂O may come from the reaction of monomer NO and surface nitrogen:



A monomer NO adsorption and desorption at higher temperature is another route for the NO detected:



In the literature it was believed (24) that NO dimer or dinitrosyl is adsorbed on the CUS of Mo. From our results the reduced Mo₂N has a stronger ability to produce NO, N₂, and N₂O than the evacuated sample. These facts make us believe that on the reduced sample more CUS exist than on the evacuated sample. This is consistent with our speculation that more severe reduction will induce more CUS.

As reviewed by Oyama (22), molybdenum nitride is produced by dissolving nitrogen atoms into the lattice of the Mo metal. As a result the Mo-Mo bond expands from 272 to 417 pm to induce a *d* band contraction and an increase of the density of states at the Fermi level of the Mo atoms, leading to the resemblance of nitride to the Group VIII metals in electronic, magnetic, and catalytic properties. Our TPD results prove that Mo nitride has similar properties in NO adsorption to that of Group VIII metals.

3.6. NO on H₂-Preadsorbed Mo₂N

A H₂-TPD was performed to provide a background for the TPD experiment of NO on H₂-preadsorbed Mo₂N. The passivated γ -Mo₂N was first reduced in flowing H₂ at 673 K for 2 h and then cooled to room temperature, also in flowing H₂, so that hydrogen was adsorbed on the sample. The TPD run was started after the H₂ was pumped out. The results are shown in Fig. 5. Three H₂ ($m/e=2$) desorption peaks at 443, 543, and 723 K were resolved, corresponding to three types of adsorbed hydrogen at different sites.

On the basis of the peak temperature and peak intensity shifts under different heating rates, Choi *et al.* (18) grouped the hydrogen adsorption sites on γ -Mo₂N into three types: low-energy surface sites (π_L), high-energy surface sites (π_H), and subsurface sites (π_S). Following their grouping we can attribute the 443 K desorption to be from the π_L sites, the 543 K one from the π_H sites, and the 723 K

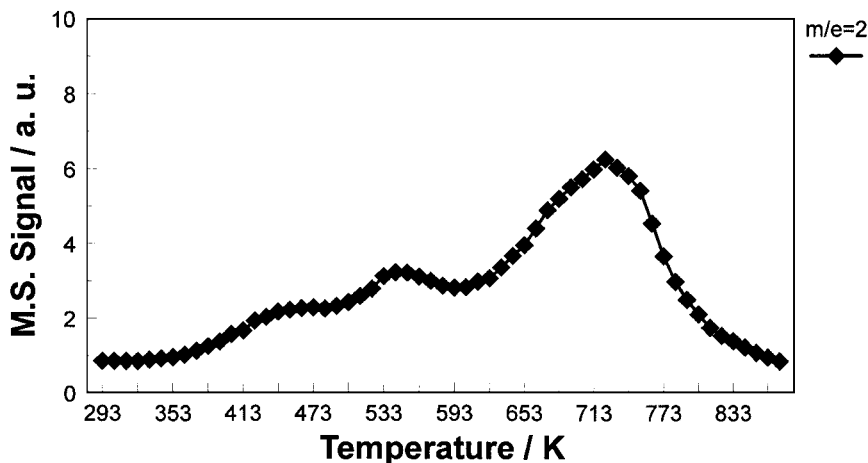


FIG. 5. TPD profiles of H₂ adsorbed at 673 K on reduced Mo₂N.

one from the π_S sites. Similar observation of hydrogen desorption was made in our group (37), where a hydrogen migration between different sites was suggested as follows. On an Mo₂N sample there are various sites for hydrogen adsorption with different adsorption energies. The sites with higher adsorption energies are not accessible for hydrogen without occupying sites with lower adsorption energy first and followed by a thermal activation. According to different conditions, hydrogen species can migrate either from low energy sites to high energy ones, or *vice versa*.

The TPD profiles after NO adsorbed on H₂-preadsorbed Mo₂N are shown in Fig. 6. This time only two H₂ desorption ($m/e=2$) peaks at 513 and 723 K are observed, instead of three as in Fig. 5. The second peak is at the same temperature as that of the highest temperature in Fig. 5, while the first peak is at a temperature (513 K) between the first two peaks in Fig. 5 (443 and 543 K). However, the peak is much closer to 543 K than to 443 K, which implies that this desorption species is from the π_H sites, but influenced by

adsorbed NO species. Two N₂ desorption peaks at 513 and 723 K, the same temperatures as those for H₂, are found. The desorption profile of H₂O shows some very broad features; however, the desorption temperatures are similar to those of N₂, with the exception of an additional desorption around 373 K. The amount of desorbed NO ($m/e=30$) decreases significantly compared with the NO desorbed from the evacuated and reduced Mo₂N (See Fig. 7). There are only two small NO desorption peaks at 363 and 503 K, which roughly coincide with the positions of the two lower temperature desorption features of NO on reduced Mo₂N (Fig. 4). The N₂O ($m/e=44$) desorption is much more intense than that with evacuated and reduced samples, and the peak temperature is at 523 K, 70 K lower than in the other two cases.

From the above results, it can be concluded that at least a part of the sites to adsorb NO can also adsorb hydrogen, and these active sites have a preferential adsorption for hydrogen. Once these active sites were occupied by

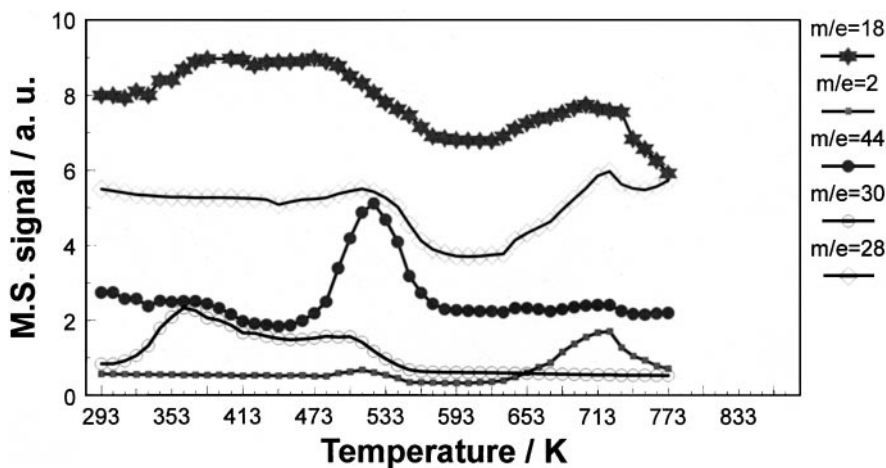


FIG. 6. TPD profiles of NO adsorbed on H₂-preadsorbed Mo₂N.

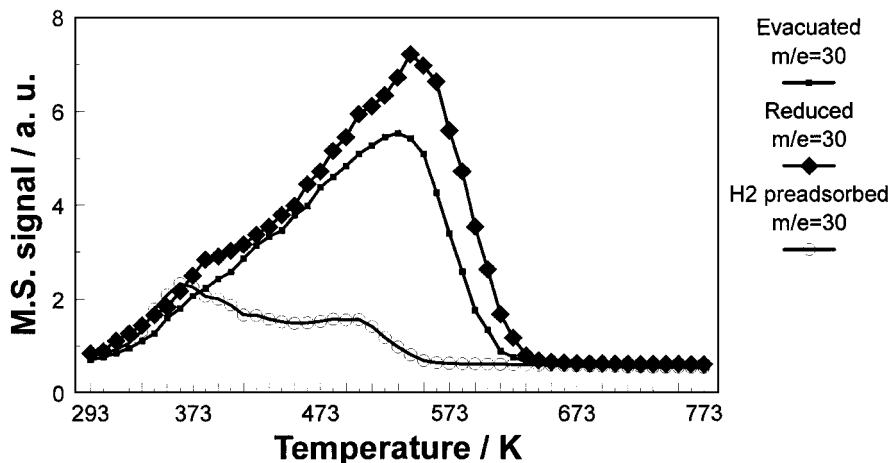
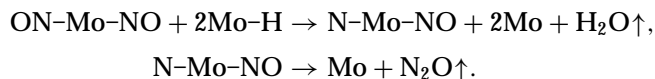


FIG. 7. A comparison of NO desorption profiles of NO adsorbed on evacuated, reduced and H₂-preadsorbed Mo₂N.

hydrogen, the adsorbed hydrogen could not be displaced by NO, consequently the highest NO desorption is missing in Fig. 6. The quantitative analysis in Subsection 3.7 can show this more clearly.

By scrutinizing the desorption features in Fig. 6 quite a few interesting phenomena can be discovered. First, there is a simultaneous disappearance of hydrogen desorption from the π_L sites and appearance of water at around 373 K. It is reasonable to suggest that the hydrogen adsorbed on the π_L sites reacts with surface oxygen originated from NO decomposition, so that all the hydrogen at the π_L sites is consumed. Second, there are H₂O, N₂, N₂O, and H₂ desorption peaks at around 500 K. We can successfully explain this by using the concept of hydrogen reverse migration (37). We think that the hydrogen adsorbed at π_L sites is the species active to react with other surface species directly if the sample temperature is adequate. However, hydrogen species adsorbed at π_H and π_S sites are held by stronger Mo-H bonds than at π_L sites, which are therefore inert to reactions with other surface species. At around 500 K the π_H hydrogen may reversely migrate (or spillover) back to the π_L sites, where they are reactive enough to react with surface O to produce water, with surface N to produce NH₃ which in turn decomposes to release N₂ and H₂, and with NO in dimer or dinitrosyl states by taking one oxygen atom from this species to form water and N₂O:



Thus the easier formation of N₂O on the H₂-preadsorbed sample is addressed, taking water formation with active hydrogen as the driving force. Then, water, N₂, and H₂ are found to desorb at 723 K coincidentally, too, which can also be easily explained by suggesting that the π_S hydrogen reversely migrates back to the π_L sites, where again it reacts

with surface O to form water and with surface N to form NH₃ which further produces N₂ and H₂. There is no more NO in dimer or dinitrosyl state to react with for the formation of N₂O at this temperature. Finally the decrease of the amount of hydrogen desorbed from the H₂-preadsorbed surface can be explained by part of hydrogen being consumed in the aforementioned reactions. However, a quantitative analysis is necessary to clear the relations between the surface species; the results are mentioned in the next section.

3.7. Quantitative Analysis of the Desorption Features

A quantitative analysis has been made to inspect the amounts of species released in Figs. 1, 3, 4, 5, and 6, whose results are tabulated in Table 2. From our volumetric adsorption measurements (38) the coverage of hydrogen on the surface of Mo₂N is around 10%, which is consistent with the literature (13). Based on this we took the H₂ desorption peak area as that correspondent to $\theta = 0.1$, and calculated all the other coverages, taking into account of the relative sensitivity factors of the relevant species (39). The factor 2 for N₂ and N₂O in the fourth column is from the consideration that for the formation of each molecule of molecular nitrogen or nitrous oxide two nitrogen atoms are needed, which are from two NO molecules adsorbed. From these results there are several points to be noted. First, after NO dosed onto hydrogen preadsorbed sample the hydrogen desorption detected is only a half as much as that from the sample with pure H₂ dosage. This has proven our assumption that some hydrogen can be knocked off by the adsorption of NO. Second, the NO desorption amount from the reduced sample is almost twice as much as that from the evacuated sample, which means much more Mo CUS can be created by hydrogen reduction than simple evacuation. Furthermore the amount of NO desorbed from the reduced sample is larger than either hydrogen or CO from

TABLE 2
Results of the Quantitative Analysis for the Species Released in Figs. 1, 3, 4, 5, and 6

Adsorbate	Sample treatment	Ads. T (K)	Peak area (a.u.)	Coverage (%)	Figure
H ₂	673 K red. 2 h	673	H ₂ : 1	10	5
¹³ CO	673 K red. 2 h	RT	¹³ CO: 1.47 (98.5%) ¹³ CO ₂ : 0.023 (1.5%)	14.9	1
NO	773 K evac. 1 h	RT	NO: 0.675 (53.0%) N ₂ × 2: 0.560 (42.4%) N ₂ O × 2: 0.087 (6.6%)	13.2	3
NO	673 K red. 2 h	RT	NO: 0.869 (38.1%) N ₂ × 2: 1.225 (53.7%) N ₂ O × 2: 0.186 (8.2%)	22.8	4
H ₂ + NO	673 K red. 2 h	H ₂ : 673 K NO: RT	H ₂ : 0.112 (22.8%) H ₂ O: 0.380 (77.2%) NO: 0.186 (24.1%) N ₂ × 2: 0.264 (34.2%) N ₂ O × 2: 0.322 (41.7%)	H ₂ : 4.9 NO: 7.7	6

the same kind of sample, indicating that there are special sites unique for NO adsorption. This may partly be due to the dissociation of NO upon adsorption. Finally, one thing we are not sure of is the difference in the NO coverages on the reduced sample (0.228) and the hydrogen preadsorbed sample (0.077). Even taking account of all the sites hydrogen occupies in the latter, there is still a surplus of 0.1. Perhaps the existence of hydrogen affects in a more significant way than simply by blocking the sites for NO adsorption, or perhaps the dissociation of NO which in our case cannot be efficiently measured plays an important role.

4. SUMMARY

Obviously from our results the aggressive adsorption of Mo toward CO is modified by nitridation. This is what we like to see, and from the mainly molecular CO adsorption Mo₂N shows properties similar to those of the Group VIII metals. There are both molecular and dissociative NO adsorption on the Mo₂N, which also resembles the properties of the Group VIII metals. Three types of sites to adsorb NO with different adsorption energies exist with the reduced Mo₂N sample; these, together with the sites to adsorb CO, are supposed to be the Mo CUS which are formed during reduction. From the literature these kinds of sites are suggested to be responsible for the hydrogenation and hydrotreating reactivities (22–24). Nitrous oxide is formed from NO in dimer or dinitrosyl state by dropping an oxygen atom. We cannot exclude the possibility that N₂O is formed from the reaction between surface NO and surface N, so far. After hydrogen adsorption at 673 K there are three types of desorptions from the sample, which can be assigned to be from the π_L , π_H , and π_S sites, corresponding to low-energy surface, high-energy surface, and subsurface sites, respectively. It seems that only the hydrogen adsorbed on

the π_L sites is active to the reactions with surface O, N, and NO in dimer or dinitrosyl state, while hydrogen adsorbed on the other two types of sites should migrate back to the π_L sites before it can react with other surface species. The surface hydrogen can promote the formation of N₂O by, as suggested tentatively, taking one oxygen atom from NO in dimer or dinitrosyl state to form water. Based on this we take the desorption of N₂O as a reaction-controlled process, which means that once there is N₂O on the surface it will be desorbed, as the desorption temperature for N₂O is much lower than the formation temperature. This is consistent with the literature that the adsorption of N₂O on transition metals is weak (40). Our quantitative analysis shows that the adsorption of NO can knock off some hydrogen preadsorbed, but not all of them; that the number of Mo CUS created after hydrogen reduction is much larger than that after pure evacuation; and that the adsorption of hydrogen, CO, and NO is not always at the same sites.

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