

Surface Sites of Alumina-Supported Molybdenum Nitride Characterized by FTIR, TPD-MS, and Volumetric Chemisorption

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The surface state and active sites of a fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ were investigated by FTIR, volumetric chemisorption, and TPD-MS techniques. It has been found that adsorption properties of CO on the fresh sample are quite different from those of the reduced passivated one. For reduced passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$, the IR spectrum of adsorbed CO shows that a band at $\sim 2180\text{ cm}^{-1}$ together with two weak bands at 2100 and 2035 cm^{-1} appear, suggesting that the Mo^{4+} cation is predominant on the surface; namely, the surface is in oxynitride form. However, for the fresh sample, adsorbed CO gives two characteristic IR bands at 2045 and 2200 cm^{-1} , respectively, corresponding to the adsorbed CO on the molybdenum and the nitrogen sites, forming linearly adsorbed CO and NCO species. From the band position of adsorbed CO, the surface molybdenum atoms are slightly positively charged, i.e., in a state of $\text{Mo}^{\delta+}$ ($0 < \delta < 2$). The assignment of the band at 2200 cm^{-1} to NCO species (CO adsorbed on N site) was further confirmed by TPD-MS and volumetric chemisorption. TPD-MS shows two CO desorption peaks at 373 and ca. 473 K , indicating two different CO adsorption sites on the catalyst. The volumetric chemisorption proves that the CO uptake increases significantly when the passivated sample is nitrated at 723 K and above, compared with the case of the reduced sample. These results suggest that not only Mo sites in low valences are present on the surface of fresh Mo nitride, but also nitrogen sites are present and so active that can react with CO to form surface NCO species.

1. Introduction

Recent years, molybdenum nitrides have attracted much attention because they show catalytic properties resembling group VIII metals in a number of hydrogen involved reactions. For example, molybdenum nitride has excellent catalytic activities in NH_3 synthesis,¹ ethane hydrogenolysis,² CO hydrogenation,^{3,4} and hydrotreating (HDN, HDS)^{4–7} reactions, etc. Molybdenum nitrides supported on oxides with high surface area have also been prepared and were tested for many hydrotreating reactions, such as HDN of quinoline,³ carbazole,⁸ and pyridine,⁹ and HDS of dibenzothiophene^{10,11} and thiophene.¹² It was found that the activities of supported Mo nitrides for HDN of pyridine were superior to that of commercially sulfided Ni–Mo hydrotreating catalyst and comparable to those of unsupported Mo nitrides.⁹

Although molybdenum nitride exhibits good catalytic performance, its surface active sites and catalytic nature have not been well understood. This is partly because of the difficulty of characterizing the nitride using spectroscopy techniques. For example, infrared spectroscopy is a powerful technique to characterize the surface active sites; however, it is hard to obtain an infrared spectrum for nitride because nitride is infrared opaque. IRAS and EELS techniques can be applied to the study of the interactions between probe molecules and model Mo nitrides, so-called nitride overlayers, but it is not easy to achieve for the nitride overlayers by annealing to higher temperatures due to the facile recombination of nitrogen atoms to desorb as

molecular nitrogen as demonstrated for $\text{N}/\text{Mo}(110)$,¹³ and besides, the studies on single crystals may not reveal the complexity of powder nitride or supported nitride.

IR spectroscopy combined with adsorption of probe molecules can be used to study the surface sites of supported molybdenum nitride because transmittance IR spectroscopy is feasible for the supported Mo nitride. CO is one of the most frequently used probe molecules to study the nature of catalysis and adsorption states of a solid surface. From the IR spectrum of adsorbed CO, it is possible to know the surface state and active sites of a catalyst. Aegerter et al.¹² first reported the IR spectra of CO adsorbed on passivated $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ and $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$. When passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ was activated with H_2 at 750 K for 2 h , a broad band at 2165 cm^{-1} of adsorbed CO was observed. When the activated sample was treated in a mixture of thiophene and hydrogen, the IR spectrum of adsorbed CO indicated that the surface of the nitride particles was partially sulfided. Their results suggest that the nitride surface is very active. However, because freshly prepared nitrated samples are rapidly oxidized when they are exposed to air, they must be passivated using a O_2/He ($< 1\% \text{ O}_2$) mixture in order to avoid the violent oxidation. Unfortunately, the passivation procedure still causes a dramatic change of the nitride surface, i.e., from nitride to oxynitride or to oxygen-covered nitride. Therefore, the surface of the nitride sample has been changed by the oxygen introduced in the passivation procedure, so it is impossible to obtain the surface information of a real nitride from a passivated sample.

To understand the surface chemistry and catalysis nature of a nitride, it is absolutely necessary to obtain the surface information of a real nitride catalyst instead of the oxynitride. Thus, an in situ study of a fresh sample, i.e., nitrated sample without meeting oxygen, has been highly expected. In this

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TABLE 1: Summary of the XPS Results of Passivated Mo₂N/Al₂O₃ Catalyst

| Mo loading (wt %) | N/Mo | binding energy (eV) and the percentages of the Mo species | | | | | |
|----------------------|------|---|------------------------|--------------------------|------------------------|--------------------------------------|------------------------|
| | | Mo ⁶⁺ (54.1%) | | Mo ⁴⁺ (34.4%) | | Mo ^{δ+} (0 < δ < 4) (11.5%) | |
| | | Mo(3d _{5/2}) | Mo(3d _{3/2}) | Mo(3d _{5/2}) | Mo(3d _{3/2}) | Mo(3d _{5/2}) | Mo(3d _{3/2}) |
| 10 | 0.68 | 232.6 | 235.8 | 230.7 | 233.9 | 229.0 | 232.2 |

paper, we report the results of CO and H₂ adsorption on fresh Mo₂N/Al₂O₃ sample using FTIR, TPD-MS, and volumetric chemisorption. For the first time, we found that the IR spectrum of adsorbed CO on the fresh Mo₂N/Al₂O₃ is totally different from those on the passivated-Mo₂N/Al₂O₃ and reduced passivated-Mo₂N/Al₂O₃, which have been well characterized in the literature. For fresh Mo₂N/Al₂O₃, CO is adsorbed not only on surface molybdenum atoms but also on surface active nitrogen atoms forming linearly adsorbed CO and NCO species, respectively.

2. Experimental Section

2.1. Catalyst Preparation. A MoO₃/Al₂O₃ sample with Mo loading of 10 wt % was prepared by incipient wetness impregnation of γ-Al₂O₃ (*S*_{BET} = 230 m²/g) with aqueous solution of (NH₄)₆Mo₇O₂₄, followed by a drying overnight at 393 K and a calcination at 773 K for 4 h. A Mo₂N/Al₂O₃ catalyst was prepared by temperature-programmed reaction of MoO₃/Al₂O₃ with ammonia. The temperature was increased from room temperature to 573 K in 0.5 h and from 573 to 973 K in 7 h, and then the temperature was maintained at 973 K for an additional 2 h. The nitrated sample was cooled to room temperature in flowing ammonia and then passivated in a stream of 1% O₂/N₂ so as to avoid violent oxidation. The as-prepared sample is called passivated Mo₂N/Al₂O₃.

2.2. XRD and XPS Measurements. Crystalline phases of alumina-supported nitride were detected by X-ray diffraction using the packed powder method, on a Rigaku Rotaflex Ru-200B diffractometer and Cu Kα radiation ($\lambda = 1.5418$ Å). An XPS experiment was carried out using an SSX-100 type 206 (Surface Science Instruments) spectrometer with an aluminum anode at 10 kV and 15 mA.

2.3. FT-IR Studies. Haddix et al. has reported that air-exposed unsupported γ-Mo₂N sample can be renitrated by simply heating in flowing ammonia at 973 K for 1 h, and the procedure did not affect the BET surface area, the crystal structure, and the H₂ uptake characteristics.¹⁴ In this work, a passivated sample was pressed into a self-supporting wafer (ca. 10 mg/cm²). The wafer was put into a quartz IR cell with CaF₂ windows and nitrated again in flowing ammonia in the IR cell. The temperature of the sample was increased from room temperature to 573 K in 0.5 h and from 573 K to required temperatures at a heating rate of 1 K/min, and then the temperature was maintained at the given temperature for 1 h. The sample nitrated in the IR cell without exposure to air is called a fresh sample or fresh nitride, while the passivated Mo₂N/Al₂O₃ reduced with H₂ is referred to as the reduced passivated sample. In a separate experiment, MoO₃/Al₂O₃ was nitrated in an IR cell, and the same results of CO adsorption were obtained as that for the sample from the nitrating of a passivated Mo₂N/Al₂O₃. Three series of experiments were performed: (1) The as-prepared fresh sample was evacuated at 773 K for 1 h, and subsequently the sample was cooled to room temperature and exposed to 10 Torr of CO (1 Torr = 133.3 N m⁻²) for IR study. (2) The as-prepared fresh sample was flushed with hydrogen at 773 K for 1 h and then evacuated at 773 K for 1 h. This sample is called a H₂-flushed sample, which was

then cooled to room temperature for CO adsorption. (3) After the fresh sample was evacuated at 773 K for 1 h, it was cooled to room temperature, and 100 Torr of H₂ was introduced into the system in order to investigate the influence of hydrogen adsorption on CO adsorption. The sample was maintained in H₂ at room temperature for 0.5 h, then the gas-phase H₂ was pumped out, and 10 Torr of CO was introduced. The sample after this treatment was called H₂-preadsorbed sample. All infrared spectra were collected at room temperature on a Fourier transform infrared spectrometer (Bio-Rad FTS 65A) equipped with a liquid nitrogen cooled MCT (mercury–cadmium–telluride) detector with a resolution of 4 cm⁻¹ and at 256 scans in the region 4000–1000 cm⁻¹. All the spectra given are differential spectra with the spectrum recorded before adsorption as the background. Unless otherwise indicated, the spectra were obtained after the system was evacuated at 10⁻⁵ Torr.

2.4. Volumetric Chemisorption. CO volumetric chemisorption was conducted at the same vacuum system as that for the IR study. A 100 mg passivated Mo₂N/Al₂O₃ was loaded into a removable U-shaped quartz reactor, which can be isolated using stopcocks. Before the chemisorption measurement, the sample was reduced or nitrated at various given temperatures as described in subsection 2.3, evacuated for 1 h, and cooled to room temperature. For CO adsorption, the conventional adsorption and back-adsorption method was employed at room temperature, and the amount of chemisorbed CO was taken by extrapolating the linear portions of isotherms to zero pressure.¹⁵

2.5. Temperature-Programmed Desorption Mass Spectroscopy (TPD-MS). The temperature-programmed desorption (TPD) experiments were carried out in a homemade glass apparatus, in which samples can be heated, evacuated, oxidized, and reduced and gases can be dosed for adsorption.¹⁶ The reactor used in this study was a U-shaped quartz tube with a quartz frit to hold the sample. A 100 mg passivated sample was put into the reactor and treated under different conditions as required. Then it was exposed to 30 Torr of CO 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 873 K. During the TPD a small portion of the desorption products was leaked into the chamber where the mass spectrometer was housed, 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, 14, 15, 16, 17, 18, 28, and 44 were monitored simultaneously.

3. Results

3.1. XRD and XPS Results. The passivated Mo₂N/Al₂O₃ catalyst (Mo loading: 10 wt %) showed only broad XRD peaks which were very difficult to be distinguished from those of alumina itself. γ-Mo₂N crystallites can only be observed for higher Mo loading materials (Mo loading > 20 wt %). The results suggest that the small particles of Mo₂N are well dispersed on the support for low Mo loading materials.

Table 1 lists a summary of XPS results of passivated Mo₂N/Al₂O₃ catalyst. It can be found that Mo⁶⁺, Mo⁴⁺, and Mo^{δ+} (0

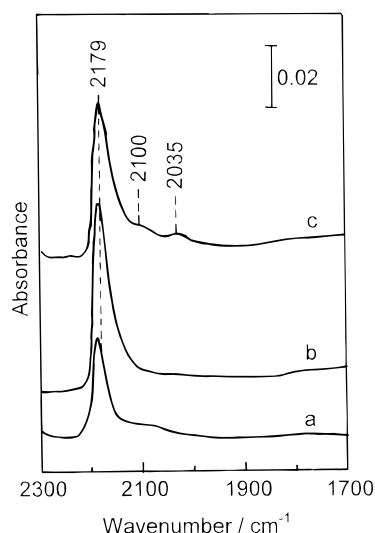


Figure 1. IR spectra of CO adsorbed at room temperature on reduced passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$. The reduction temperature is (a) 673, (b) 773, and (c) 873 K.

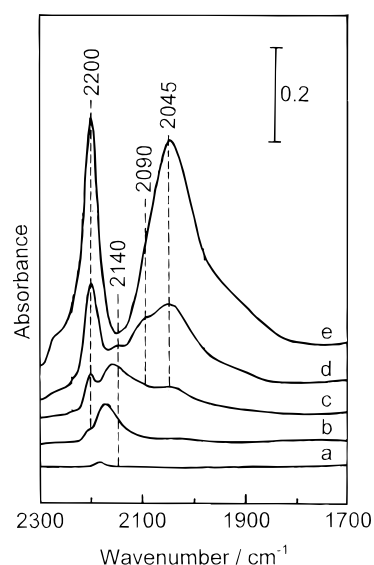


Figure 2. IR spectra of CO adsorbed at room temperature on fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ nitrided at various temperatures: (a) 573, (b) 673, (c) 723, (d) 773, and (e) 873 K.

$< \delta < 4$) cations, with a binding energy of $\text{Mo}3d_{5/2}$ at 232.6, 230.7, and 229.0 eV, respectively, are present for the passivated samples. This is consistent with the unsupported Mo nitrides,^{16–18} which revealed that the passivated procedure strongly modified the surface of Mo nitride, and accordingly, the passivated samples are mainly oxynitrides rather than nitrides.

3.2. IR Results. **3.2.1. CO Adsorption on Reduced Passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$.** IR spectra of CO adsorbed on passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ reduced at various temperatures are given in Figure 1. An IR band at 2187 cm^{-1} can be seen for CO adsorption on the sample reduced at 673 K. At 773 K, the band of adsorbed CO shifts slightly from 2187 to 2184 cm^{-1} . This spectrum is similar to that reported by Aegerter et al.¹² with the exception that the band position reported was at 2165 cm^{-1} . The band further shifts downward to 2179 cm^{-1} , and two weak bands at 2102 and 2035 cm^{-1} appear when the sample was reduced at 873 K. This indicates that more surface sites for CO adsorption are generated owing to the deeper reduction. An IR band appears at around 2180 cm^{-1} is attributed to linearly adsorbed CO on Mo^{4+} sites;^{19–23} thus, our results suggest that most

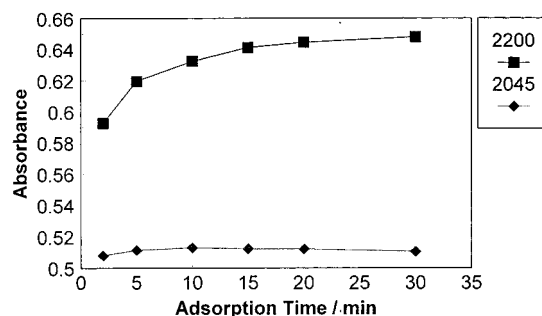


Figure 3. Intensities of the bands at 2045 and 2200 cm^{-1} as a function of adsorption time ($P_{\text{CO}} = 10\text{ Torr}$).

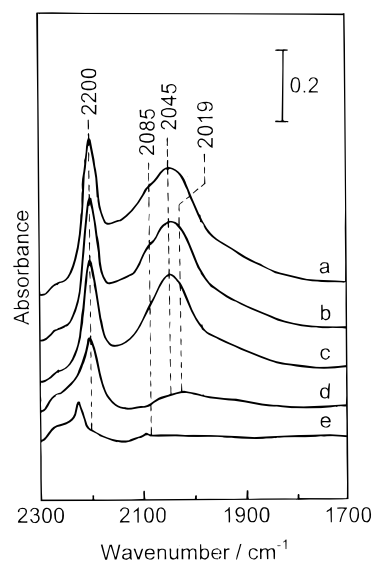


Figure 4. IR spectra of CO adsorbed at room temperature on fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ nitrided at 873 K as a function of temperatures: (a) 10 Torr of CO; (b) evacuation to 10^{-2} Torr; (c) evacuation to 10^{-5} Torr; (d) evacuation at 423 K; and (e) evacuation at 573 K.

surface Mo sites on the reduced passivated sample are still in a high valence state (Mo^{4+}); namely, the sample is still in the oxynitride form, even though it was reduced at 873 K.

3.2.2. CO Adsorption on Fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$. Figure 2 exhibits the spectra of CO adsorbed on fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ nitrided at various temperatures. For the sample nitrided at 573 K, only a weak band appears at 2184 cm^{-1} for CO adsorption. This band hardly changes except for a small shift from 2184 to 2173 cm^{-1} when the sample is nitrided at 673 K. However, after a nitriding at 723 K, the IR spectrum of the adsorbed CO shows a dramatic change (Figure 2c); four IR bands are observed at 2200, 2110, and 2045 cm^{-1} . For the sample nitrided at 773 K, the four IR bands appear at 2200, 2140, 2090, and 2045 cm^{-1} (Figure 2d). The two bands at 2140 and 2090 cm^{-1} decline in intensity while the two bands at 2200 and 2045 cm^{-1} grow remarkably. These changes are totally different from those for reduced passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ (see Figure 1). After being nitrided at 873 K, mainly two IR bands are left for the adsorbed CO—a strong band at 2200 cm^{-1} and a broad band at 2045 cm^{-1} —and their intensities become considerably strong compared with those for $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ nitrided at 773 K.

The changes of the band intensities of 2045 and 2200 cm^{-1} as a function of adsorption time can be seen from Figure 3. With the increase of adsorption time, the intensities of the two bands increase. However, the intensity of the 2200 cm^{-1} band increases more pronouncedly than that of the 2045 cm^{-1} band with increasing adsorption time, indicating that the two bands

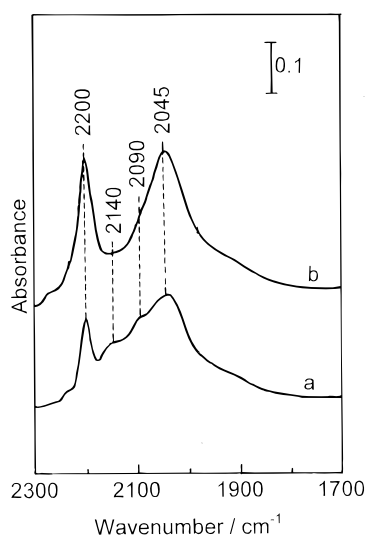


Figure 5. IR spectra of CO adsorbed at room temperature on fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ nitrided at 773 K (a) and 873 K (b) followed by flushing with hydrogen at 773 K for 1 h.

are correlated with two different kinds of adsorbed CO species. Figure 4 shows IR spectra reflecting the stability of the adsorbed CO on the fresh sample nitrided at 873 K. The intensities of the two bands at 2200 and 2045 cm^{-1} are retained under evacuation at room temperature, indicating that the adsorbed species are stable. Both the bands at 2200 and 2045 cm^{-1} are stable until warming to 373 K. When the sample is heated to 423 K under vacuum, the band at 2045 cm^{-1} diminishes while the band at 2200 cm^{-1} can be still seen even though the temperature is elevated to 673 K. This band disappears only when the temperature is increased to 773 K. This result also clearly manifests that the two bands at 2045 and 2200 cm^{-1} represent two kinds of species formed from the CO adsorption on the fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ because their stabilities are quite different.

3.2.3. CO Adsorption on H_2 -Flushed and H_2 -Preadsorbed $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ Nitrided at Various Temperatures. Figure 5 shows the IR spectrum of adsorbed CO on fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ pre-flushed with hydrogen at 773 K for 1 h. In contrast with the spectra in Figure 2, the intensity ratio of the band at 2200 cm^{-1} to 2045 cm^{-1} decreases somewhat, but no shifts are observed for these two bands. This suggests that the hydrogen pretreatment simply reduces the surface sites available for forming the species having the IR band at 2200 cm^{-1} , whereas those with IR band at 2045 cm^{-1} were not or less affected.

Figure 6a shows the IR spectrum of adsorbed CO on a hydrogen-preadsorbed sample. The fresh sample was nitrided at 773 K and then exposed to H_2 at room temperature. Three weak IR bands at 3346, 3259, and 3159 cm^{-1} are observed after the H_2 was introduced (see Figure 6A, curve a). These bands can be attributed to the stretching vibrations of N–H bonds which are formed via the reaction of adsorbed hydrogen with surface active nitrogen sites. Figure 6b gives the IR spectrum of CO adsorbed on the H_2 -preadsorbed sample nitrided at 873 K. Similar results as observed in Figure 5 are obtained; that is, the intensity ratio of the band at 2200 cm^{-1} to 2045 cm^{-1} decreases when the fresh sample is either exposed to H_2 at room temperature or preflushed with H_2 at 773 K before CO adsorption. But when CO was adsorbed first, the bands are not affected by a followed admission of hydrogen. This obviously means that the surface sites are common for hydrogen and CO adsorption, while CO is more strongly adsorbed than hydrogen.

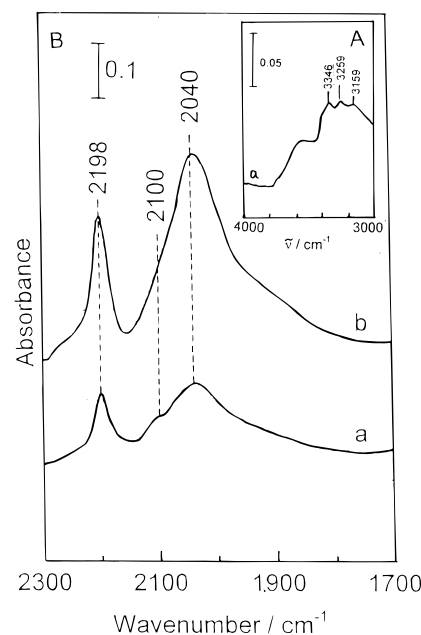


Figure 6. (A) IR spectra of H_2 adsorbed at room temperature on fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ nitrided at 773 K. (B) IR spectra of CO adsorbed at room temperature on H_2 preadsorbed $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ nitrided at 773 K (a) and 873 K (b).

TABLE 2: CO Uptake Amount ($\mu\text{mol/g}$) of Reduced Passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ and Fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$

| treatment conditions | CO total uptake amount | CO irreversible uptake amount | CO/Mo ^a |
|----------------------|------------------------|-------------------------------|--------------------|
| reduction at 673 K | 111.8 | 58.2 | 0.056 |
| reduction at 873 K | 165.5 | 64.5 | 0.062 |
| nitridation at 673 K | 368.7 | 225.3 | 0.22 |
| nitridation at 723 K | 517.0 | 374.0 | 0.36 |
| nitridation at 773 K | 600.8 | 473.3 | 0.45 |
| nitridation at 873 K | 648.0 | 535.5 | 0.51 |

^a Calculated as adsorbed CO atoms to molybdenum atoms, but this ratio is not equal to the percentage exposed of Mo available for CO adsorption because N atoms that can adsorb CO should be considered for the fresh samples.

3.3. Volumetric Chemisorption. Table 2 lists the CO uptake amount of passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ treated under various conditions. The CO uptake amount is about 60 $\mu\text{mol/g}$ when the sample was reduced at 673 or 873 K, which is consistent with Aegerter et al.¹² However, for fresh sample, the CO uptake amount increases considerably, especially when it was nitrided at 723 K and above. These results are in good agreement with IR results in Figure 2, which lead us to the conclusion that in situ nitridation strongly increases the CO adsorption ability of Mo nitride.

3.4. TPD-MS Results. Figure 7 shows the TPD results of CO adsorbed on reduced passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ and fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ nitrided at various temperatures. A small CO desorption peak at 373 K appears for the sample reduced at 873 K, while for the fresh samples the amount of desorbed CO is greatly increased, in consistent with the IR and volumetric chemisorption results. When the sample was nitrided at 723 K and above, a shoulder peak at about 473 K besides the peak at 373 K appears, and the area of the shoulder increases with elevation of the nitriding temperature. This indicates that the two peaks represent two kinds of adsorbed CO. Combining with Figure 4, we can deduce that the peak at 373 K corresponds to the species with an IR band at 2045 cm^{-1} , and the shoulder at 473 K corresponds to the species with an IR band at 2200 cm^{-1} . At temperatures higher than 723 K, another desorption

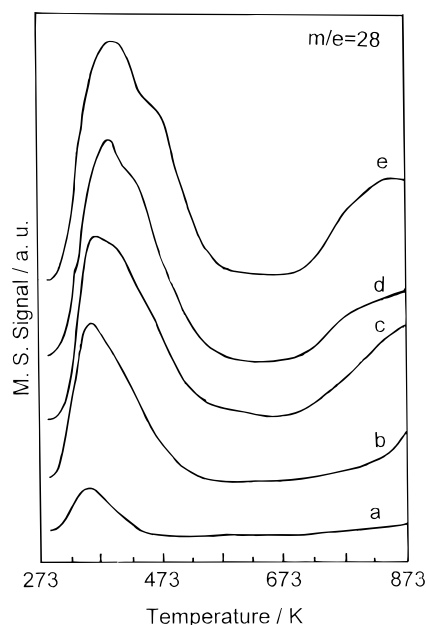


Figure 7. TPD profiles of CO adsorbed at room temperature on reduced passivated $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ (reduced at 873 K) (a) and on fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ at 673 K (b), 723 K (c), 773 K (d), and 873 K (e), respectively.

peak appears, and the area of this peak also increases with nitriding temperature. Taking account of the parallel signals of $m/e = 12$ and 14, the desorption peak of $m/e = 28$ at high temperatures can be attributed to the desorption of nitrogen, which is from the recombination of nitrogen atoms in the molybdenum nitride.^{16,18}

4. Discussion

4.1. Assignment of the IR Bands at 2045 and 2200 cm^{-1} . CO adsorption^{19–23} has been well used to investigate the surface states of partially reduced and sulfided molybdenum supported on alumina or other supports. These studies could be good reference for the assignment of the IR spectra of adsorbed CO on molybdenum nitride. Linearly carbonyl species coordinated to Mo sites with valence $\geq +3$ exhibit $\text{MoC}-\text{O}$ stretching frequencies higher than that of free CO molecule (2143 cm^{-1}). In contrast, those held by Mo with valence $< +3$ show $\nu_{\text{MoC}-\text{O}}$ frequencies lower than 2143 cm^{-1} .¹⁹ A band around 2100 cm^{-1} is commonly attributed to the adsorbed CO on $\text{Mo}^{\delta+}$ ($0 < \delta < 4$),^{19,20} while a band at $2070\text{--}2050 \text{ cm}^{-1}$ can be assigned to adsorbed CO on Mo^{2+} .^{12,21,22} Müller et al.²¹ studied adsorbed CO at low temperatures on sulfided $\text{Mo}/\text{Al}_2\text{O}_3$. CO adsorption on the surface sites created by reductive elimination of sulfur species forms a complex that is characterized by a band at ca. 2100 cm^{-1} , which was assigned to the $\text{Mo}^{2+} \leftarrow \text{CO}$ adsorption complex located at the edge position of the MoS_2 slabs. Also, a shoulder band at ca. $2060\text{--}2070 \text{ cm}^{-1}$ appeared after a mild reduction (453 K). Combining with their TPRS results, they attributed this band to a second $\text{Mo}^{2+} \leftarrow \text{CO}$ complex, and the Mo^{2+} is located at corners. DeCanio and Storm²² studied the freshly calcined $\text{Mo}/\text{Al}_2\text{O}_3$ samples reduced at 673 K by CO adsorption. They assigned the band at 2175 cm^{-1} to CO adsorbed on Mo^{4+} , the band at 2050 cm^{-1} to adsorbed CO species on Mo^{2+} , and the band at 1997 cm^{-1} to adsorbed CO on Mo^0 .

Adsorbed CO on a clean $\beta\text{-Mo}_2\text{C}$ foil gave rise to a ν_{CO} band at 2069 cm^{-1} , and this band was assigned to adsorbed CO on Mo^{2+} . A shoulder band at $\sim 2125 \text{ cm}^{-1}$ was observed when

CO was introduced to the molybdenum carbide foil which was exposed to O_2 prior to CO.²⁴ This shoulder is presumably associated with CO adsorbed on an oxidized Mo site. For the 20% $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ catalyst investigated by Aegerter et al.,¹² a band of adsorbed CO was observed at 2178 cm^{-1} with a shoulder at 2060 cm^{-1} when CO was adsorbed at 130 K. The appearance of the band at 2178 cm^{-1} suggests the presence of oxidized Mo sites on the surface of the catalyst, and the band at 2060 cm^{-1} was attributed to as Mo^{2+} , i.e., carbided Mo. In summary, the IR bands at $2070\text{--}2050 \text{ cm}^{-1}$ resulting from CO adsorption on reduced or carbided Mo catalysts can be attributed to adsorbed CO on Mo^{2+} ,^{12,21,22} while an IR band at $2025\text{--}2000 \text{ cm}^{-1}$ was assigned to linearly adsorbed CO on fully reduced molybdenum, namely, Mo^0 .^{20,22}

In this study, two characteristic IR bands at 2045 and 2200 cm^{-1} appear when CO is adsorbed on the fresh sample nitrided at temperatures at and above 723 K. Their intensities are enhanced significantly with the increase of nitriding temperature of the sample. A blank experiment was conducted for CO adsorption on alumina pretreated with ammonia as done for the supported material. At room temperature, no IR bands of adsorbed CO were detected for the alumina which was nitrided at 873 K. Also, our TPD and IR results showed that no ammonia remained on the fresh samples after they were evacuated at 773 K for 1 h.²⁵ Therefore, the effects of support and residue NH_3 on the adsorbed CO species can be excluded; that is, the two bands at 2045 and 2200 cm^{-1} observed for fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ are only correlated with the adsorbed CO on Mo_2N phase. From DTA results,²⁵ the nitriding reaction is initiated at about 723 K, so that it is also reasonable to assign the two bands to adsorbed CO on Mo_2N .

As discussed above, the IR band at 2045 cm^{-1} can be safely assigned to the linearly adsorbed CO on the surface molybdenum atom of the fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$, which may be positively charged, i.e., $\text{Mo}^{\delta+}$ ($0 < \delta < 2$). For the band at 2200 cm^{-1} , we assign it to the NCO species, as a result of CO adsorbed on surface N sites.²⁶ Based on the survey of the literature, there are three possible assignments of the band at 2200 cm^{-1} : CO adsorbed on Mo^{5+} sites,¹⁹ CO adsorbed on cus Al^{3+} ,¹⁹ and NCO species.²⁶ However, the CO adsorption on either Mo^{5+} or cus Al^{3+} sites of Al_2O_3 is very weak, and the adsorbed CO cannot be stable under evacuation even at room temperature.¹⁹ Also, CO adsorption on Mo^{n+} ($n > 0$) is usually rather weak; therefore, obviously the strong band at 2200 cm^{-1} cannot be assigned to the CO adsorbed on Mo^{n+} or Al^{3+} . As summarized by Nakamoto,²⁶ the NCO group is very stable, and its frequency is in the right region at 2200 cm^{-1} as we observed. There are also a number of studies convincing that the band around 2200 cm^{-1} is from adsorbed NCO species.^{27–29} The reasoning is also based on the only possible reaction at room temperature between CO and active N sites available on the fresh nitride. Therefore, the band at 2200 cm^{-1} is only due to NCO species, which is actually formed when CO reacts with surface active nitrogen atom on the fresh $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ sample. The results also suggest that a considerable amount of nitrogen atoms are present on the surface top of molybdenum nitride, and the nitrogen atoms are in the highly active form which may also play an important role in the catalysis of molybdenum nitride.

One may argue that the band at 2200 cm^{-1} might be assigned to the CN species. However, the $\nu(\text{CN})$ of free CN^- is 2080 cm^{-1} . Upon coordination to a metal, the $\nu(\text{CN})$ shifts to higher frequencies, but it is lower than 2200 cm^{-1} .²⁶ On the other hand, even though the species is cyanate N-bonded to Mo, it means that adsorbed CO must undergo a dissociation to C and

TABLE 3: Frequencies and Assignments of Surface Species Formed by CO Adsorption on Reduced Passivated Mo₂N/Al₂O₃ and on Fresh Mo₂N/Al₂O₃

| treatment conditions | IR bands, ^a cm ⁻¹ | assignment |
|----------------------|---|------------------------------------|
| reduction at 673 K | 2187(w) | Mo ⁴⁺ (CO) |
| reduction at 773 K | 2184(w) | Mo ⁴⁺ (CO) |
| reduction at 873 K | 2179 (w) | Mo ⁴⁺ (CO) |
| | 2100 (vw) | Mo ³⁺ (CO) |
| | 2034 (vw) | Mo ^{δ+} (CO) |
| nitridation at 573 K | 2184 (w) | Mo ⁴⁺ (CO) |
| nitridation at 673 K | 2200 (sh) | NCO |
| | 2173 (w) | Mo ⁴⁺ (CO) |
| nitridation at 723 K | 2200 (s) | NCO |
| | 2157 (s), 2110 (w) | Mo ³⁺ (CO) ₂ |
| | 2045 (b) | Mo ^{δ+} (CO) |
| nitridation at 773 K | 2200 (s) | NCO |
| | 2149 (w), 2093 (w) | Mo ³⁺ (CO) ₂ |
| | 2045 (b) | Mo ^{δ+} (CO) |
| nitridation at 873 K | 2200 (s) | NCO |
| | 2117 (vw), 2086 (vw) | Mo ³⁺ (CO) ₂ |
| | 2045 (b) | Mo ^{δ+} (CO) |

^a s = strong; b = broad; sh = shoulder; w = weak; and vw = very weak. $0 < \delta < 2$.

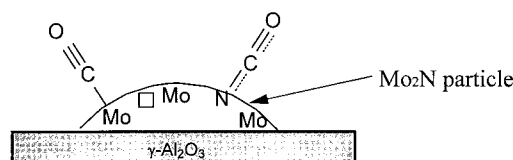
O. The produced O atoms must oxidize the neighboring Mo site, resulting in a higher Mo valence state; as a consequence, the IR spectra of adsorbed CO will show a remarkable change. But we never observe this change in the spectra of adsorbed CO.

Mo atoms with different environments may exist on the surface of the fresh samples, leading to nonstoichiometric complex sites able to chemisorb CO differently.¹⁹ For Mo nitrides, coordinatively unsaturated sites (cus) of Mo with nitrogen and/or oxygen deficiencies can be produced by nitridation and evacuation at high temperatures, and CO can adsorb on these sites. But when Mo atoms are in full nitride form, they should be in the valence of 0–4.¹⁷ CO adsorption on Mo cations in this valence will give IR bands at ca. 2100–2000 cm⁻¹ rather than at 2200 cm⁻¹,^{19–23} even though environments of Mo cations may be very different; i.e., usually the frequencies of adsorbed CO on Mo are more affected by Mo valence than its surrounding environments.

The IR spectra of CO adsorbed on a H₂-flushed or -preadsorbed sample further confirm our assignments of the two bands at 2200 and 2045 cm⁻¹. The band intensity of 2200 cm⁻¹ decreases dramatically while the band at 2045 cm⁻¹ remains unchanged when the fresh catalyst was treated with hydrogen at 773 K or H₂ preadsorbed at room temperature. This is because a treatment with hydrogen at high temperatures removes part of the surface active nitrogen atoms; as a result, the band intensity of the NCO species declines because this species is formed through the reaction between CO and the surface active nitrogen atom. While the preadsorbed hydrogen can occupy or/and react with surface active nitrogen sites as deduced from Figure 6, accordingly the number of surface active nitrogen sites left for CO adsorption is reduced.

The assignments for CO adsorption on samples treated under various conditions are listed in Table 3. On the basis of the assignments, a schematic model of surface Mo site and N site on fresh Mo₂N/Al₂O₃ detected by CO adsorption is proposed as shown in Figure 8.

Based on the above assignments, our TPD-MS results can be well explained. The CO desorbed with peak temperature at 373 K is attributed to linearly adsorbed CO on Mo^{δ+} ($0 < \delta < 2$), while the CO desorbed with a shoulder peak at 473 K is associated with CO adsorbed on N sites.

**Figure 8.** A schematic model of surface Mo site and N site on fresh Mo₂N/Al₂O₃ detected by CO adsorption.

4.2. Surface Sites Produced by Reduction or Nitridation of the Passivated Mo₂N/Al₂O₃. A passivation treatment of nitride is basically a slow oxidation process which leads to the incorporation of oxygen into the nitride. Elemental analysis shows that the amount of oxygen present in the passivated Mo₂N is estimated to be as high as 19% of the total amount of nitrogen present in pure Mo₂N.³⁰ Markel and Van Zee⁵ concluded that passivation produces a protective, amorphous surface oxide slightly greater than one monolayer thick. Also, Wise and Markel³¹ have shown that passivated γ-Mo₂N is stabilized by an amorphous oxide surface layer like that of MoO₂. Whatever the real passivated layer is, it is doubtless that the passivation procedure has caused a dramatic change of the nitride, i.e., from nitride to oxynitride or oxygen covered nitride. This is confirmed by our IR results of CO adsorption on a passivated Mo₂N reduced at various temperatures. The IR results of adsorbed CO on reduced passivated-sample and fresh sample show that CO adsorption on the reduced passivated Mo₂N/Al₂O₃ sample is more analogous to that of reduced MoO₃/Al₂O₃ but different from that of fresh Mo₂N/Al₂O₃.

A study²³ of CO adsorption on reduced MoO₃/Al₂O₃ concluded that Mo⁴⁺ cation was mainly produced when MoO₃/Al₂O₃ was reduced at the temperatures from 573 to 773 K. No adsorbed CO on Mo⁰ was detected for MoO₃/Al₂O₃ reduced at temperatures below 973 K. A significant exposure of fully reduced Mo atoms on MoO₃/Al₂O₃ was detected only after a reduction above 973 K.²⁰ In Figure 1, the IR band at 2179 cm⁻¹ indicates that CO is adsorbed mainly on Mo⁴⁺ for the reduced passivated Mo₂N/Al₂O₃ reduced at 873 K. Apparently, the result is totally different from that obtained by CO adsorption on fresh Mo₂N/Al₂O₃ sample (Figure 2). So we can conclude that the surface of reduced passivated Mo₂N/Al₂O₃ is in a highly oxidic form, i.e., the Mo⁴⁺ cation is predominant on the surface, and it is not really a molybdenum nitride although some publications believed it was.

The adsorbed CO on fully reduced Mo can be removed by a prolonged evacuation;²⁰ however, the CO held by fresh Mo₂N/Al₂O₃ is very stable. It strongly suggests that CO adsorption behavior on the surface Mo of fresh nitride is more like that on group VIII metals rather than on Mo metal in nature. Although it has been reported that some transition metal nitrides and carbides show similar electronic, magnetic, and catalytic properties to noble metals such as Pt,³² no IR evidence was reported for checking the similarity in surface electronic property between the two types of catalysts. Our IR results unambiguously prove that a fresh molybdenum nitride resembles group VIII metals in CO adsorption, implying that the surface electronic property of fresh Mo nitride is very close to that of group VIII metals.

Studies of CO adsorbed on Mo(100) single-crystal plane revealed that CO initially adsorbed in molecular form at low temperature, but the adsorbed CO completely dissociated upon heating to 270 K.^{32–35} The dissociation was hindered in the presence of carbon layer.³⁶ From CO-TPD results, Lee et al.¹⁵ found that CO was the only desorbed species for Mo₂C/Al₂O₃ catalyst, while CO₂ was observed for reduced Mo/Al₂O₃. Wang et al.²⁴ found that CO only partially dissociated on β-Mo₂C.

Our CO-TPD results also indicate that the majority of CO adsorbed molecularly on Mo₂N/Al₂O₃ catalyst; no desorption peak of CO₂ was detected, which suggests the aggressive adsorption of molybdenum toward CO is modified to a much milder manner by nitridation.

4.3. The Surface Percentage of Mo Atoms Available for CO Chemisorption. The amount of irreversibly adsorbed CO is estimated by extrapolating the linear portion of the two isotherms of the total and reversibly adsorbed CO. The CO/Mo ratio was calculated by dividing the amount of irreversibly adsorbed CO by the amount of Mo atoms in the catalyst, as listed in Table 2. However, this ratio is not equal to the percentage exposed of Mo that can adsorb CO because for fresh samples, the N sites that adsorbed CO should be considered. For fresh Mo₂N/Al₂O₃ sample, assuming that a surface Mo site and a surface nitrogen site can only accommodate one CO molecule (on-top adsorption), respectively, then the percentage exposed of Mo that can adsorb CO is $2/3$ times the value of "CO/Mo". Thus, the percentage of Mo atoms available for CO adsorption is calculated to be 34% for the sample nitrided at 873 K. It is worth noting that this value is much higher than that of highly reduced MoO₃/Al₂O₃ studied by Burwell and co-workers.³⁷ By reducing MoO₃/Al₂O₃ at 1223 K by H₂, they achieved 25% exposure for the 7.4 Mo % catalyst, wherein each CO is assumed to occupy 1.5 Mo sites.

The increase of Mo exposure for the fresh sample can be explained as follows. First, the nitriding procedure can cause a significant reduction in crystallite and a considerable increasing surface area of Mo₂N.³⁸ Second, for the alumina-supported Mo nitride, some Mo₂N may exist as two-dimensional, raftlike domains, as assumed by Colling and Thompson,⁹ and the two-dimensional domains have a high percentage of exposed Mo atoms.

The average particle sizes D_p of Mo₂N can be estimated using stoichiometries of CO chemisorption, the so-called titration method.¹⁵ Assuming spherical particles and a site density of 10^{15} cm⁻², D_p is given by $6/\rho S_g$, where ρ is the solid density and S_g denotes the specific surface area of Mo₂N excluding the area of alumina support. For the fresh sample nitrided at 873 K, assuming one Mo and one N atom adsorbed one CO molecule, respectively, it can be calculated that the average particle size of Mo₂N is ca. 3 nm.

4.4. Adsorption of Hydrogen. The adsorption of H₂ on unsupported Mo₂N has been well-studied.^{17,39,40} However, the hydrogen adsorption on supported Mo₂N has not been investigated. It has been reported that hydrogen can be adsorbed on Mo sites with nitrogen deficiencies for unsupported Mo₂N.¹⁴ Also, a heterolytic dissociation mechanism of H₂ adsorption was assumed as that of hydrogen adsorption on MoS₂, but no direct evidence was given.³⁹ Our IR results clearly demonstrated that preadsorption of H₂ on the fresh Mo₂N/Al₂O₃ hinders the CO adsorption, particularly decreasing the band intensity at 2200 cm⁻¹, which had been assigned to the adsorbed CO on the nitrogen site. IR bands are also observed in the 3000–3600 cm⁻¹ region due to the stretching vibration of ν_{N-H} when H₂ was preadsorbed at room temperature. These bands can be attributed to the stretching vibrations of the N–H bond. These results supply the direct proof for that H₂ reacted with surface active N sites to form N–H species. This also suggests that the surface nitrogen on fresh molybdenum nitride is very reactive.

5. Conclusion

CO and H₂ adsorptions on fresh Mo₂N/Al₂O₃ and reduced passivated Mo₂N/Al₂O₃ were investigated using FT-IR, TPD-

MS, and volumetric chemisorption techniques. For reduced passivated sample, the Mo⁴⁺ cation is predominant on its surface; i.e., its surface is in the oxynitride form. While for the fresh sample, both Mo ^{δ +} ($0 < \delta < 2$) and N sites are mainly on the surface as probed by adsorbed CO giving two characteristic IR bands at 2045 and 2200 cm⁻¹, and the two bands are assigned to linearly adsorbed CO on Mo sites and NCO species, respectively. The NCO species is formed when CO reacts with the surface N sites on the fresh Mo₂N/Al₂O₃. Unlike adsorbed CO on reduced passivated Mo₂N/Al₂O₃, the adsorbed CO on Mo nitride is very stable, behaving similarly to that on group VIII metals. Flushing the fresh sample with hydrogen at high temperatures or preadsorbing hydrogen can reduce the N sites capable of adsorbing CO, thus decreasing the amount of NCO species. Volumetric chemisorption and TPD-MS results confirm that the amount of adsorbed CO on the fresh Mo₂N/Al₂O₃ is much higher than that on passivated Mo₂N/Al₂O₃, indicating that the nitridation process creates more active sites for CO adsorption.

Our results also suggest that the in situ FT-IR studies on fresh nitrides are very important to the understanding of real surface of nitrides, while the studies on passivated nitrides cannot give true information of nitride, instead giving information on oxynitride or oxygen-covered nitride.

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