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Sulfur Effect on Mo_2N/γ-Al_2O_3 Catalyst Studied by *in Situ* FT-IR Spectroscopy

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The sulfur effect of both thiophene and H_2S on Mo_2N/γ-Al_2O_3 catalyst has been characterized by *in situ* **FT-IR spectroscopy. CO adsorption was used to probe the effect of thiophene and H_2S on the surface of the Mo_2N/γ-Al_2O_3 catalyst. The adsorbed thiophene has strong electronic interaction with the Mo_2N/γ-Al_2O_3 catalyst and does not sulfide the surface of the catalyst at temperatures below 673 K. While in the presence of H_2, the surface of the Mo_2N/γ-Al_2O_3 catalyst can be partially sulfided by thiophene at temperatures as low as 373 K, simultaneously the adsorbed thiophene is decomposed or hydrodesulfurized on the catalyst. H_2S has stronger interaction with the Mo_2N/γ-Al_2O_3 catalyst than thiophene does and can slightly sulfide the catalyst surface even at room temperature. The catalyst surface is deeply sulfided by an H_2S/H_2 mixture at temperatures even about 373 K. The surface of the sulfided nitride catalyst can be only partially regenerated by a renitridation using NH_3 at 873 K, indicating that some formation of sulfur species on the nitrided catalyst is irreversible. However, the nitrided surface can be completely regenerated when the catalyst is first oxidized and then renitrided. The sulfur effect on a reduced passivated Mo_2N/γ-Al_2O_3 catalyst was also investigated.** © 2000 Academic Press

Key Words: **molybdenum nitride; thiophene; H_2S; FT-IR spectroscopy; CO adsorption; sulfur effect; hydrodesulfurization.**

INTRODUCTION

In recent years, transition metal nitrides have attracted much attention because they show catalytic properties resembling group VIII metals in a number of hydrogen-involved reactions. Especially, they have potential applications in both hydrodenitrogenation (HDN) (1–8) and hydrodesulfurization (HDS) (1, 3, 9–14) processes. However, transition metal nitrides are found to be sensitive to sulfur species. Ramanathan *et al.* (1) confirmed the formation of a sulfide phase after HDS reaction on several bimetallic oxynitrides, including NbMo–O–N, CrMo–O–N, MoW–O–N, etc. In a study of liquid phase quinoline HDN over nitrides, Schlatter and Oyama (8) found that the reactivity of Mo_2N was similar to that of MoS_2 in the presence of CS_2. Aegerter *et al.* (9) found by IR spectroscopy that alumina-supported molybdenum nitride became sulfided at HDS temperatures. The XPS data (15) of a nitrided Mo/Al_2O_3 catalyst used in dibenzothiophene HDS reaction showed that the surface of the spent catalyst was covered with sulfur that reduced the activity of the nitrided catalyst down to that of the sulfided catalyst. Choi *et al.* reported that in the presence of H_2S, the product selectivity shifted significantly toward hydrogenation products during the HDN of pyridine over Mo_2N catalyst (16).

However, it is noted that the results mentioned above were concentrated on passivated nitrides, i.e., fresh nitrides passivated with 1% O_2/N_2 and then reduced with H_2 before use. Little attention has been paid to fresh nitrides (17–19). It is known that the passivation procedure causes a dramatic change in the nitride surface, i.e., from nitride to oxygen-covered nitride. So the results do not reflect the truth about fresh nitrides. Therefore, it is of significance to study how a fresh nitride works under the reaction conditions. Thiophene is a typical representative of sulfur-containing hydrocarbons in hydrotreating reactions and H_2S is one of the final products from the HDS of sulfur-containing compounds, so it is necessary to study the influence of thiophene and H_2S on the surface property of nitride catalysts in order to get insight into the sulfur effect on the catalytic performance.

IR spectroscopy, combined with the adsorption of probe molecules, is a powerful technique to characterize the surface active sites. CO is a probe molecule popularly used to study the surface states and active sites of catalysts and has been demonstrated to be feasible for the study of fresh nitride catalyst (20, 21) and sulfide catalyst (22). In our previous study (20), we found that the pretreatment of passivated Mo_2N/γ-Al_2O_3 with H_2 or NH_3 leads to reduced passivated or renitrided Mo_2N/γ-Al_2O_3, respectively. The reduced passivated and fresh Mo_2N/γ-Al_2O_3 catalysts show absolutely different IR spectra of adsorbed CO, indicating the different properties of their surface sites. Therefore, it is desirable to investigate the influence of sulfur species on the two kinds of catalysts.

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In this work, the characteristics of differently pretreated passivated Mo_2N/γ-Al_2O_3 catalyst with respect to the sulfur effect were described. The adsorption/desorption/reaction behaviors of thiophene on Mo_2N/γ-Al_2O_3 catalyst were studied by IR spectroscopy combined with CO adsorption. The influences of thiophene and H_2S on the surface of Mo_2N/γ-Al_2O_3 catalyst and regeneration of the sulfided surface were investigated in detail. Our results show that thiophene or H_2S can easily sulfide the Mo_2N/γ-Al_2O_3 catalyst even at relatively low temperatures when H_2 is present. The sulfided catalyst can be fully recovered only when the catalyst is first oxidized and then renitrided. Similar experiments for reduced passivated Mo_2N/γ-Al_2O_3 catalyst were also studied.

EXPERIMENTAL

Catalyst Preparation

The MoO_3/γ-Al_2O_3 sample with Mo loading of 10 wt% was prepared by incipient wetness impregnation of γ-Al_2O_3 ($S_{BET} = 172\ m^2/g$) with an aqueous solution of $(NH_4)_6Mo_7O_{24}$, followed by drying at 393 K overnight and calcination at 773 K for 4 h. The Mo_2N/γ-Al_2O_3 catalyst, i.e., nitrided catalyst, was prepared by the temperature-programmed reaction of MoO_3/γ-Al_2O_3 with ammonia as follows: The temperature was increased from room temperature (RT) to 623 K in 1 h and from 623 K to 973 K in 6 h, and then the temperature was maintained at 973 K for another 2 h. Passivated Mo_2N/γ-Al_2O_3 sample was prepared from the nitrided sample which was passivated at RT in a stream of 1% O_2/N_2 so as to avoid the violent oxidation of the freshly prepared nitride.

XRD Measurement

Crystalline phases of passivated Mo_2N/γ-Al_2O_3 were detected by X-ray diffraction using the packed powder method, on a Rigaku Rotaflex Ru200B diffractometer with Cu *Kα* radiation ($\lambda = 1.5418$ Å).

FT-IR Studies

The pretreatment of samples for IR studies was done as follows: A passivated sample was pressed into a self-supporting wafer (ca. 15 mg/cm^2) and put into a quartz IR cell with CaF_2 windows to renitride in flowing ammonia. The sample was heated from RT to 623 K in 30 min, then to 723 K in 100 min, further from 723 K to 873 K in 75 min, and finally held at this temperature for 60 min. The sample renitrided in the IR cell is called Mo_2N/Al_2O_3 or nitrided sample, while the passivated sample treated with H_2 at 773 K for 2 h is denoted as reduced passivated Mo_2N/γ-Al_2O_3. The same IR spectra in the ν_{CO} region were obtained from CO adsorption on the samples from the nitridation of MoO_3/γ-Al_2O_3 and the renitridation of passivated Mo_2N/γ-Al_2O_3. This demonstrates that the renitridation procedure mentioned above can produce Mo_2N/γ-Al_2O_3 quite different from the passivated nitride. To save time, we use passivated Mo_2N/γ-Al_2O_3 instead of MoO_3/γ-Al_2O_3 as the starting sample in the IR cell, because it takes longer to nitride the MoO_3/γ-Al_2O_3 sample. Haddix *et al.* (23) have also reported that air-exposed γ-Mo_2N sample can be renitrided by simply treating it in flowing ammonia at 973 K, and the procedure did not affect the BET surface area, the crystal structure, and the H_2 uptake characteristics.

The as-prepared sample was evacuated at 773 K for 60 min, and subsequently cooled to RT. Then three different IR experiments were carried out as follows: (1) About 1 Torr thiophene was introduced to the IR cell for thiophene adsorption. (2) The sample was exposed to a mixture of 10 Torr (1 Torr = 133.3 N m^{-2}) CO and 5 Torr thiophene or 25 Torr H_2S for coadsorption study. (3) Thiophene (5 Torr) or an H_2/thiophene mixture (30/5 Torr) was introduced into the IR cell for 30 min and the cell evacuated at RT. Then the sample was outgassed at different temperatures (373, 473, 573, and 673 K) for 10 min. This procedure is denoted as adsorption/desorption/reaction of thiophene with the catalyst. After cooling down to RT, the sample was exposed to 10 Torr CO. (4) The sample in the IR cell was treated with a thiophene/H_2 mixture (5/500 Torr) or an H_2S/H_2 mixture (25/500 Torr) for 60 min at different temperatures (373, 473, 573, and 673 K) and then evacuated at 773 K for 20 min. Then the sample was cooled to RT and 10 Torr CO was introduced. (5) The catalyst treated by procedure (4) was again renitrided or first oxidized and then renitrided to investigate the nature of the sulfur species on the treated catalyst. Some of the treatments were also performed for the reduced passivated sample.

All infrared spectra were collected at RT on a Fourier transform infrared spectrometer (Nicolet Impact 410) with a resolution of 4 cm^{-1} and 64 scans in the region 4000–1000 cm^{-1}. All the spectra were obtained at RT after the sample was outgassed, unless otherwise indicated.

RESULTS

XRD Results

As shown in Fig. 1, the passivated Mo_2N/γ-Al_2O_3 catalyst (10 wt% Mo) (Fig. 1b) shows broad XRD peaks which make it difficult to distinguish the Mo_2N phase from γ-alumina. The diffraction patterns for Mo_2N/γ-Al_2O_3 catalyst with high Mo loading (Mo loading $\geq$20 wt%) exhibit peaks at 38.2°, 44.2°, 64.0° (shoulder), and 76.7° which are assigned to the {111}, {200}, {220}, and {311} reflections of bulk γ-Mo_2N, respectively. The results suggest that Mo_2N particles are well dispersed on the support for low Mo loading samples.

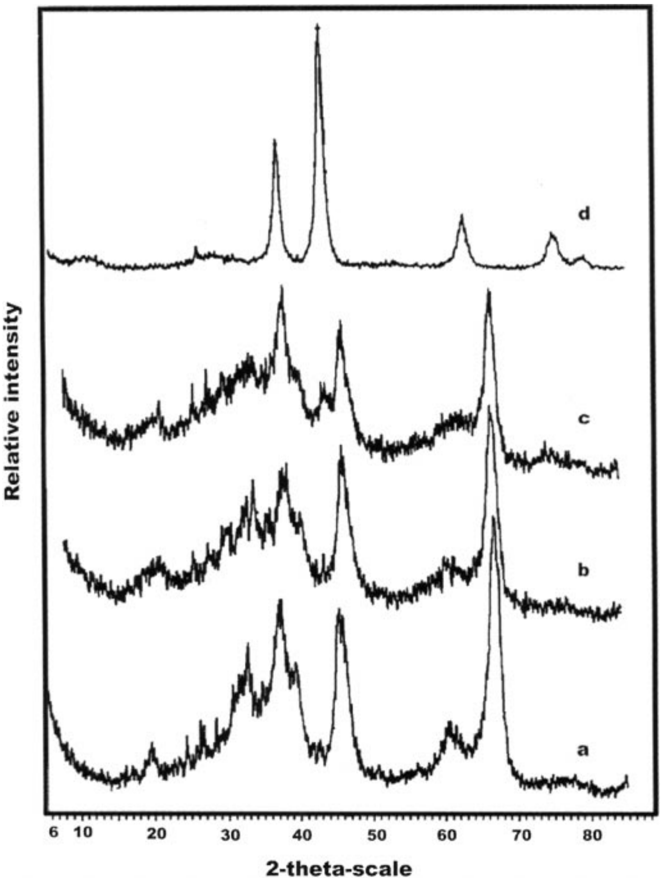

FIG. 1. XRD patterns of (a) γ-Al_2O_3, (b) passivated Mo_2N/γ-Al_2O_3 (10% Mo), (c) passivated Mo_2N/γ-Al_2O_3 (20% Mo), and (d) passivated γ-Mo_2N.

IR Results

Thiophene adsorption on Mo_2N/γ-Al_2O_3 catalyst. Figure 2 shows the IR spectra of thiophene adsorbed on Mo_2N/γ-Al_2O_3 and nitrided γ-Al_2O_3 at RT. The assignment of the labeled peaks can be found elsewhere (24). There is no apparent difference between the two IR spectra. Since the Mo loading of the used catalyst is only 10 wt%, part of the support is exposed to the adsorbate. Thus, the observed IR bands of thiophene adsorbed on Mo_2N/γ-Al_2O_3 should be attributed to the adsorbed thiophene mainly on the surface of alumina, while the IR bands of adsorbed thiophene on the Mo_2N surface of Mo_2N/γ-Al_2O_3 may be relatively weak.

Coadsorption of CO with thiophene or H_2S on Mo_2N/γ-Al_2O_3 and on reduced passivated Mo_2N/γ-Al_2O_3 catalyst. Figure 3 shows the IR spectra of CO coadsorbed with thiophene or H_2S on Mo_2N/γ-Al_2O_3 at RT. Adsorbed CO on Mo_2N/γ-Al_2O_3 gives two characteristic IR bands at 2045 and 2200 cm^{-1}, respectively, corresponding to the adsorbed CO on the surface Mo and N sites, forming linearly adsorbed CO and NCO species (20, 21). When CO adsorbed

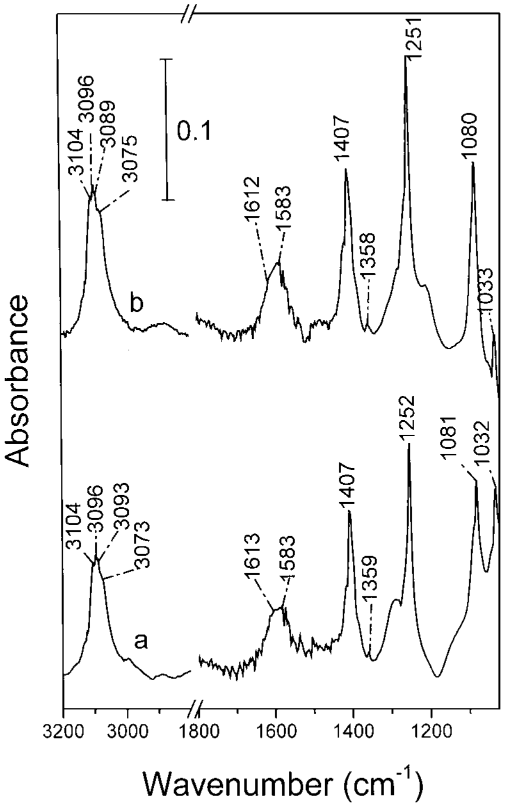

FIG. 2. IR spectra of thiophene adsorbed on (a) nitrided γ-Al_2O_3 and (b) Mo_2N/γ-Al_2O_3 catalyst.

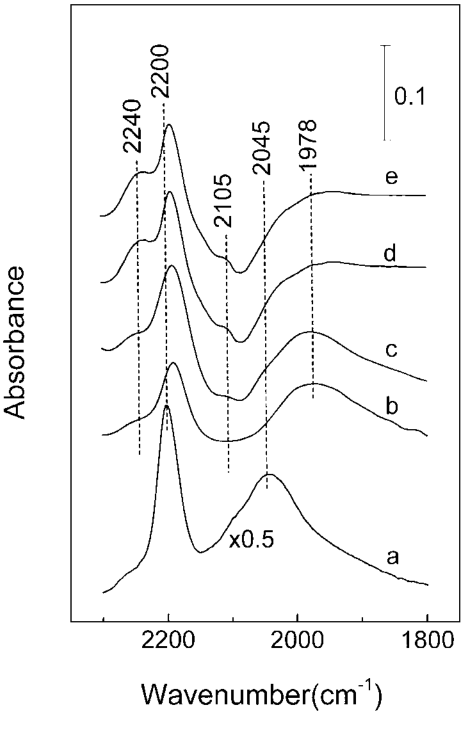

FIG. 3. IR spectra of CO adsorbed on Mo_2N/γ-Al_2O_3 catalyst: (a) CO alone; (b) thiophene preadsorbed, then CO; (c) CO preadsorbed, then thiophene; (d) H_2S preadsorbed, then CO; (e) CO preadsorbed, then H_2S.

on the catalyst preadsorbed with thiophene, the bands at 2200 cm^{-1} and 2045 cm^{-1} shift to 2190 cm^{-1} and 1978 cm^{-1}, respectively, accompanying the decrease in intensity. A shoulder band at 2240 cm^{-1} appears at the same time. The changes of the two bands are almost the same as in the case when CO is adsorbed first. This means that the surface sites of Mo_2N/γ-Al_2O_3 are common for both CO and thiophene adsorption. Thiophene can greatly influence the adsorption of CO, especially on the Mo sites. When CO coadsorbed with H_2S at RT, the 2200-cm^{-1} band shifts to 2190 cm^{-1} and the band at 2045 cm^{-1} completely disappears, accompanying the appearance of an evident band at 2240 cm^{-1} and a weak band at 2105 cm^{-1}. The assignment of the band at 2240 cm^{-1} will be discussed later. The formation of the weak band at 2105 cm^{-1} indicates the partial sulfidation of the nitride surface because this is a characteristic band of CO adsorbed on sulfided Mo catalyst and has been assigned to linearly adsorbed CO on *cus* Mo^{2+} sites (22). It seems that H_2S has strong interaction with Mo_2N/γ-Al_2O_3 and is predominately adsorbed on the catalyst so that the IR band of adsorbed CO on Mo sites vanishes.

Figure 4 exhibits the IR spectra of CO coadsorbed with thiophene and H_2S on reduced passivated Mo_2N/γ-Al_2O_3 at RT. CO adsorption on the passivated sample reduced at 773 K gives a band at 2181 cm^{-1} which has been assigned to linearly adsorbed CO on Mo^{4+} sites (9, 20). No bands are observed for CO coadsorption with either thiophene or H_2S on the reduced passivated sample. This is quite different from the case of the nitrided sample. It is obvious that thiophene and H_2S are more strongly adsorbed than CO on passivated Mo_2N/γ-Al_2O_3. This may be partly due to the fact that CO adsorption on passivated sample is weaker than that on the nitrided sample (20). It turns out that the surface sites of passivated Mo_2N/γ-Al_2O_3 are more easily affected by sulfur-containing compounds (thiophene or H_2S) than those of nitrided catalyst.

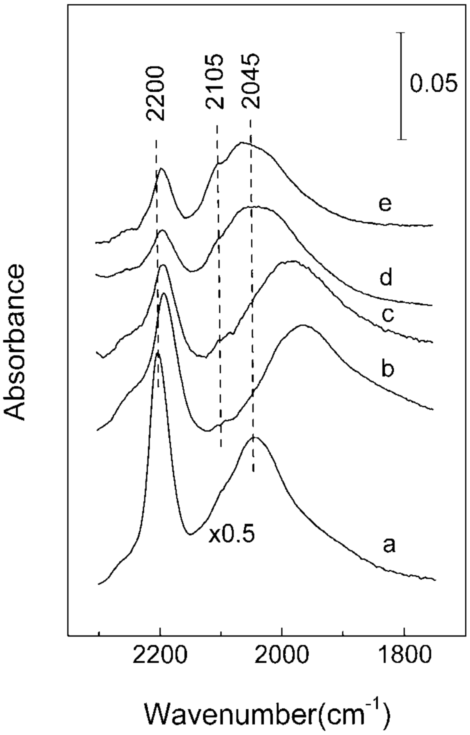

FIG. 5. IR spectra of CO adsorbed (a) at RT on Mo_2N/γ-Al_2O_3 catalyst, and on the same catalyst preadsorbed with thiophene followed by outgassing at (b) 373 K, (c) 473 K, (d) 573 K, and (e) 673 K.

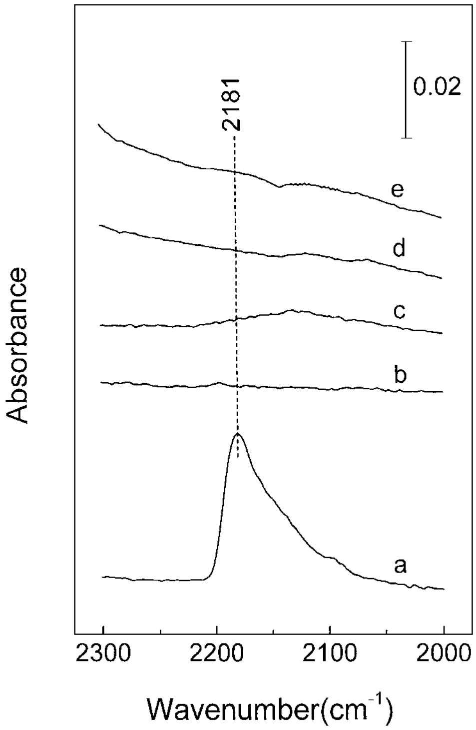

FIG. 4. IR spectra of CO adsorbed at RT on reduced passivated Mo_2N/γ-Al_2O_3 catalyst: (a) CO alone; (b) thiophene preadsorbed, then CO; (c) CO preadsorbed, then thiophene; (d) H_2S preadsorbed, then CO; (e) CO preadsorbed, then H_2S.

CO adsorption on Mo_2N/γ-Al_2O_3 pretreated with thiophene. In order to further understand the effect of thiophene on Mo_2N/γ-Al_2O_3 catalyst, the adsorption/desorption/reaction behaviors of thiophene on the catalyst were investigated. After thiophene was adsorbed on the Mo_2N/γ-Al_2O_3 catalyst and then desorbed at different temperatures, CO was adsorbed on the treated catalyst at RT to probe the changes in the adsorption sites. As shown in Fig. 5, the 2200-cm^{-1} band shifts to 2195 cm^{-1} and the 2045-cm^{-1} band to 1950 cm^{-1} when the thiophene desorption temperature is 373 K; meanwhile, their intensities decease. The 1950-cm^{-1} band shifts to 1980 cm^{-1} for thiophene desorption at 473 K. When thiophene is outgassed at 573 K, the 2195-cm^{-1} band hardly changes, while a broad IR band at 2045 cm^{-1} appears, which is almost the same as that of CO adsorbed on the Mo sites of Mo_2N/γ-Al_2O_3

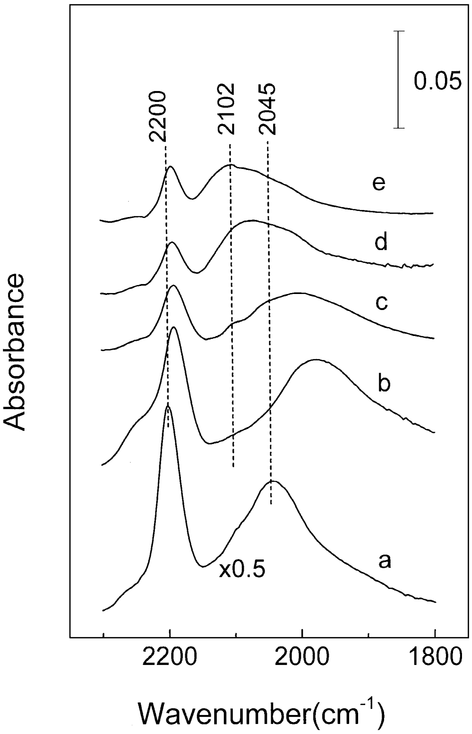

FIG. 6. IR spectra of CO adsorbed (a) at RT on Mo_2N/γ-Al_2O_3 catalyst, and on the same catalyst preadsorbed with H_2/thiophene (25/5 Torr) followed by outgassing at (b) 373 K, (c) 473 K, (d) 573 K, and (e) 673 K.

except for the declined intensity. The 2045-cm^{-1} band shows a small shift to higher frequency and a new shoulder peak at 2105 cm^{-1} appears at thiophene desorption temperatures above 573 K. No changes of the 2195-cm^{-1} band of adsorbed CO on N sites are observed. The appearance of the new IR band at 2105 cm^{-1} suggests that the surface of the sample was slightly sulfided.

Considering that H_2 is a main reactant in the HDS of thiophene, hydrogen was adsorbed on Mo_2N/γ-Al_2O_3 catalyst before thiophene adsorption, then the mixture was outgassed at RT and then at different higher temperatures. CO was introduced to probe the surface sites after the sample cooled to RT. As presented in Fig. 6, the changes in the band at 2200 cm^{-1} assigned to the adsorbed CO on N sites are almost the same as those in thiophene preadsorption alone, while the IR band of adsorbed CO on Mo sites shows some differences. When H_2/thiophene is evacuated at 373 K, the 2045-cm^{-1} band shifts to 1976 cm^{-1}, which again shifts back to 2005 cm^{-1}, and a small shoulder band at 2102 cm^{-1} appears after evacuation at 473 K. When the adsorbed H_2/thiophene is outgassed at 573 K, CO adsorption gives a main band at 2069 cm^{-1} and a shoulder band at 2102 cm^{-1}. The main band shifts to 2102 cm^{-1} for the evacuation at 673 K. These IR features are quite different from those of CO adsorbed on the nitride catalyst preadsorbed with thiophene alone. This indicates that preadsorption of H_2 can greatly affect the adsorption/desorption/reaction behaviors of thiophene on Mo_2N/γ-Al_2O_3 catalyst.

CO adsorption on Mo_2N/γ-Al_2O_3 treated with a thiophene/H_2 mixture or an H_2S/H_2 mixture at different temperatures. To investigate the sulfiding effect on Mo_2N/γ-Al_2O_3 catalyst under different conditions, the catalyst was treated with a thiophene/H_2 mixture (5/500 Torr) or an H_2S/H_2 mixture (25/500 Torr) at given temperatures for 1 h and then its surface nature was probed by CO adsorption at RT. Figure 7 exhibits the IR spectra of CO adsorbed on an Mo_2N/γ-Al_2O_3 sample treated with a thiophene/H_2 mixture. The 2200-cm^{-1} band shifts to 2195 cm^{-1} and its intensity decreases gradually with the elevated treatment temperatures and disappears when the temperature is higher than 573 K. The band at 2045 cm^{-1} shifts to higher frequencies when the treatment temperature is increased, e.g., to 2080 cm^{-1} at 373 K, to 2090 cm^{-1} at 473 K, to 2102 cm^{-1} at 573 K, and to 2105 cm^{-1} above 573 K. The results strongly suggest that the surface of the Mo_2N/γ-Al_2O_3 catalyst is significantly changed when treated with the thiophene/H_2 mixture above RT.

In addition to the changes in the surface sites of the nitrided catalyst, changes in the thiophene itself were also detected when the Mo_2N/γ-Al_2O_3 catalyst was treated with a thiophene/H_2 mixture at different temperatures. As shown

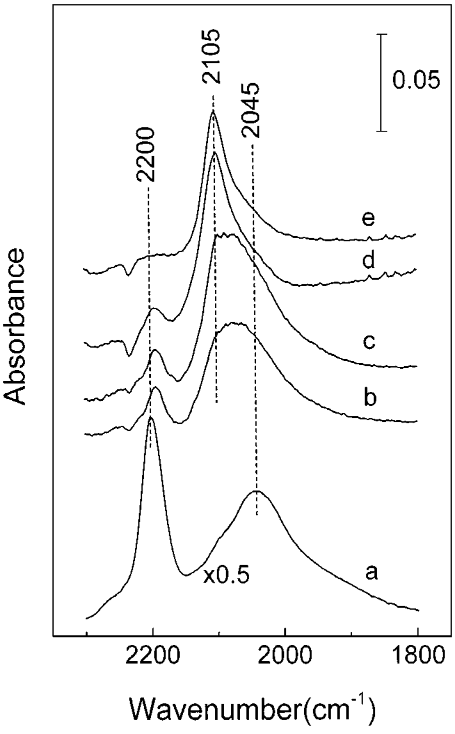

FIG. 7. IR spectra of CO adsorbed (a) at RT on Mo_2N/γ-Al_2O_3 catalyst, and on the same catalyst after it was treated with a thiophene/H_2 (5/500 Torr) mixture at (b) 373 K, (c) 473 K, (d) 573 K, and (e) 673 K for 1 h.

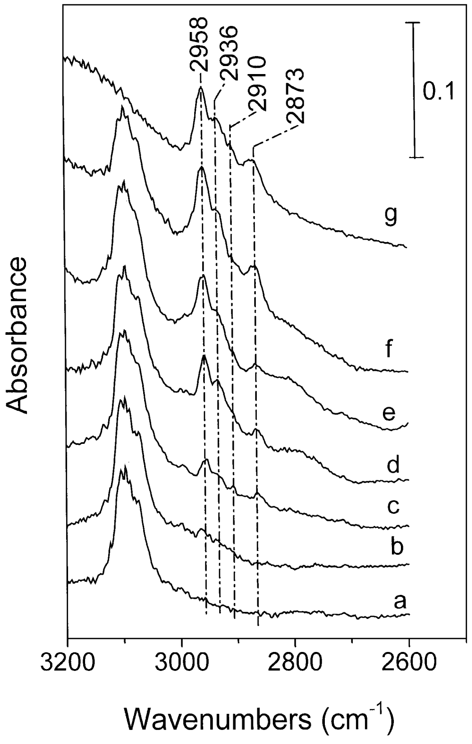

FIG. 8. IR spectra in the ν_{CH} region for (a) thiophene adsorbed on Mo_2N/γ-Al_2O_3 catalyst at RT for 1 h, and the same catalyst after it was treated with a thiophene/H_2 (5/500 Torr) mixture for 1 h at (b) RT, (c) 373 K, (d) 473 K, (e) 573 K, and (f) 673 K, and (g) evacuation of (f) at RT.

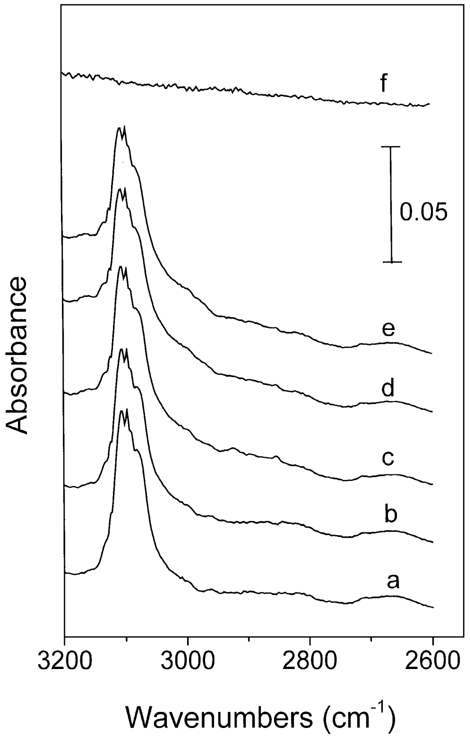

FIG. 9. IR spectra in the ν_{CH} region for thiophene adsorbed on Mo_2N/γ-Al_2O_3 catalyst for 1 h at (a) RT, (b) 373 K, (c) 473 K, (d) 573 K, and (e) 673 K, and (f) evacuation of (e) at RT.

in Fig. 8, treatment of the nitrided sample at 373 K produces four new bands at 2958, 2936, 2910, and 2873 cm^{-1} in the ν_{CH} region. Further treatment at 673 K results in only an increase in intensities. Absorbance features at 1605, 1461, 1443, and 1213 cm^{-1} are also observed. Evacuation at RT of the sample treated at 673 K produces no changes in these bands (both frequencies and intensities). These bands are similar to those observed by Tarbuck *et al.* (24) and could be assigned to strongly adsorbed hydrocarbon species on the catalyst surface. No such absorbance features are observed in the IR spectra of γ-Al_2O_3 treated with thiophene/H_2 mixture at different temperatures. The IR spectra of gas phase and adsorbed thiophene show no absorbance bands in the 2800–3000 cm^{-1} region at RT. When the Mo_2N/γ-Al_2O_3 catalyst was treated with 5 Torr thiophene at different temperatures (373, 473, 573, and 673 K) for 1 h and cooled to RT, no IR bands in the 2800–3000 cm^{-1} region were observed (shown in Fig. 9). Therefore, this implies that thiophene is reactive on the Mo_2N/γ-Al_2O_3 catalyst only in the presence of H_2 and results in some new species strongly adsorbed on the catalyst.

Figure 10 shows the influence of H_2S/H_2 treatment on the IR spectra of CO adsorbed on Mo_2N/γ-Al_2O_3. When the treatment temperature is 373 K, the 2200-cm^{-1} band shifts to 2194 cm^{-1} and becomes very weak, while the 2045-cm^{-1}

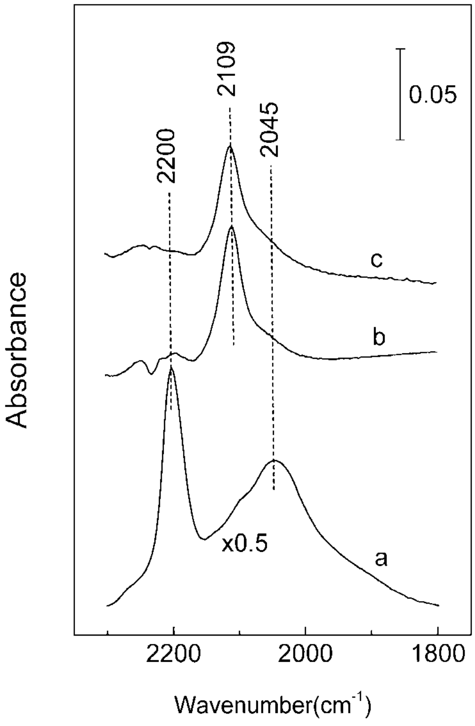

FIG. 10. IR spectra of CO adsorbed (a) at RT on Mo_2N/γ-Al_2O_3 catalyst, and on the same catalyst after it was treated with an H_2S/H_2 mixture (25/500 Torr) at (b) 373 K and (c) 473 K for 1 h.

band shifts to 2109 cm^{-1}. The 2200-cm^{-1} band disappears and the 2109 cm^{-1} does not change for H_2S/H_2 treatment at 473 K. The IR spectra of CO adsorbed on reduced passivated sample treated with an H_2S/H_2 mixture at different temperatures are given in Fig. 11. The band at 2181 cm^{-1} shifts to 2120 cm^{-1} when the treatment temperature is 373 K and above. It is clear that the surface of both the nitrided and the reduced passivated Mo_2N/γ-Al_2O_3 is easily changed by the H_2S/H_2 treatment.

Regeneration of the surface of the sulfided Mo_2N/γ-Al_2O_3 catalyst. Two different methods were used to regenerate the surface of the sulfided catalyst. After the Mo_2N/γ-Al_2O_3 catalyst was treated with a thiophene/H_2 mixture at 673 K for 1 h, the sample was renitrided with NH_3 or first oxidized in flowing O_2 at 673 K and then renitrided with NH_3. The IR spectra of CO adsorbed on the regenerated samples are shown in Fig. 12. After the catalyst was treated with thiophene/H_2 at 673 K for 1 h, CO adsorption showed one band at 2100 cm^{-1} (Fig. 12b), indicating the sulfidation of the surface. After the renitridation of the sulfided catalyst, shown as spectrum c, CO adsorption gives two main bands at 2198 cm^{-1} and 2100 cm^{-1} and one shoulder band at 2045 cm^{-1}, which indicates that the major part of the surface is still in the sulfide form. In contrast, for the sulfided catalyst oxidized prior to the renitridation, CO adsorption shows two bands at 2200 cm^{-1} and 2025 cm^{-1} (Fig. 12d), which are characteristic of CO adsorbed on Mo_2N/γ-Al_2O_3 catalyst. Obviously, the surface of the sulfided catalyst can be partly regenerated by the simple renitridation. A complete regeneration requires an oxidation of the catalyst prior to the renitridation.

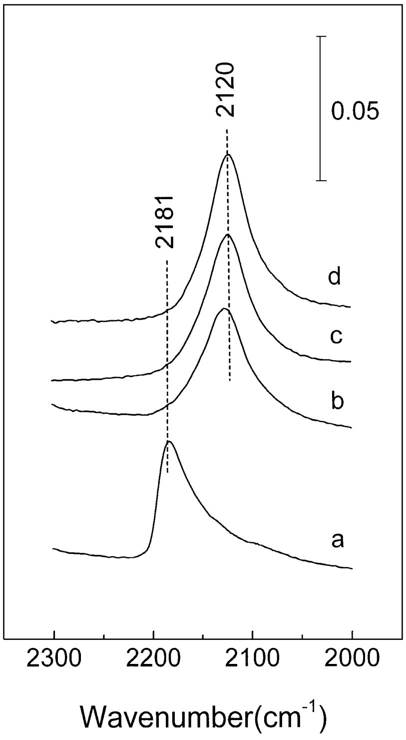

FIG. 11. IR spectra of CO adsorbed (a) at RT on reduced passivated Mo_2N/γ-Al_2O_3 catalyst, and on the same catalyst after it was treated with an H_2S/H_2 mixture (25/500 Torr) at (b) 373 K, (c) 473 K, and (d) 573 K for 1 h.

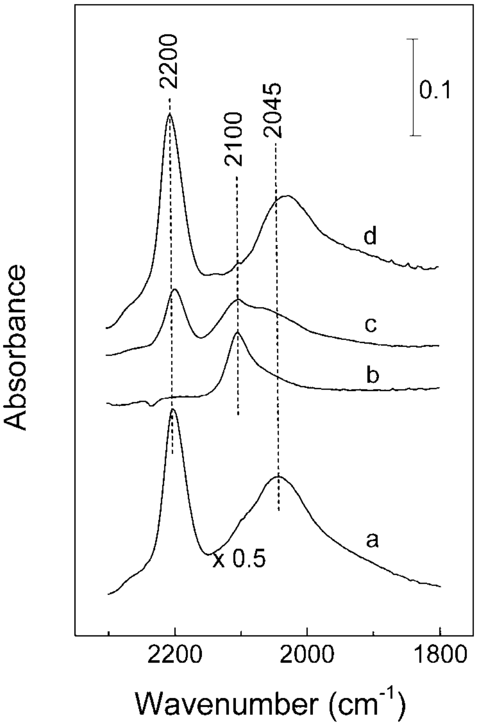

FIG. 12. IR spectra of CO adsorbed (a) at RT on Mo_2N/γ-Al_2O_3 catalyst, (b) on the same catalyst after it was treated with thiophene/H_2 (5/500 Torr) at 673 K for 1 h, (c) on the sulfided Mo_2N/γ-Al_2O_3 catalyst after a renitridation with NH_3 at 873 K, and (d) on the sulfided Mo_2N/γ-Al_2O_3 catalyst after it was regenerated by oxidation at 673 K and then renitridation at 873 K.

DISCUSSION

Adsorption/Desorption/Reaction Behaviors of Thiophene on Mo_2N/γ-Al_2O_3 Catalyst

Since there are no obvious differences between the IR spectra of thiophene adsorbed on Mo_2N/γ-Al_2O_3 catalyst and γ-Al_2O_3, the adsorption/desorption/reaction behaviors of thiophene on Mo_2N/γ-Al_2O_3 catalyst can be simply deduced from the IR features of CO adsorption. The fact that the IR band of adsorbed CO on Mo sites shifts to lower frequencies when CO is coadsorbed with thiophene (Fig. 3) reflects the weakening of the C–O bond due to the increase of electron donation from surface Mo sites. This is the evidence showing that thiophene has strong electron donation to the surface of Mo_2N/γ-Al_2O_3 catalyst. It can be explained in terms of π donation from the adsorbed thiophene to the surface Mo sites. As the properties of transition metal nitrides have been found to resemble the properties of noble metals (25), the electron donation from the adsorbed thiophene can transfer from the surface of the nitride to the coadsorbed CO. As a consequence, the IR band of adsorbed CO on the Mo sites shifts to lower frequencies. This can lead to the conclusion that adsorbed thiophene has a strong electronic effect on the catalyst surface and does not change the surface nature.

Also as shown in Fig. 5, when the adsorbed thiophene is outgassed at temperatures no higher than 573 K, no sulfide phase is formed on the surface as the IR band at 2105 cm^{-1} due to the adsorbed CO on sulfide catalyst is not observed. This suggests that the adsorbed thiophene keeps its molecular form when desorbing from the Mo_2N/γ-Al_2O_3 catalyst at temperatures no higher than 573 K. As the thiophene desorption temperature is higher than 573 K, a shoulder IR band at 2105 cm^{-1} appears; this indicates that part of the adsorbed thiophene has undergone decomposition and reaction at this temperature, forming surface sulfur-containing species, which may be responsible for the partial sulfidation of the molybdenum nitride surface.

The influence of hydrogen on the adsorption/desorption/reaction behaviors of thiophene on Mo_2N/γ-Al_2O_3 catalyst is obvious as presented in our IR spectra (comparing Fig. 6 with Fig. 5). When H_2 is preadsorbed, the desorption/reaction behavior of thiophene on Mo_2N/γ-Al_2O_3 is changed. First, the IR band of adsorbed CO on Mo sites is always at higher wavenumbers than that of thiophene preadsorbed alone. This can be attributed to two possible reasons. One is that adsorbed hydrogen inhibits the adsorption of thiophene and the other is that adsorbed thiophene desorbs and decomposes or reacts with the surface easily in the presence of hydrogen. As a result, the d–π interaction is weakened, so that the IR band of adsorbed CO on Mo sites shows a smaller shift to the lower frequency region. Second, the IR band at 2102 cm^{-1} assigned to adsorbed CO on Mo sulfide appears at lower temperatures and becomes the main band finally, different from the case with thiophene preadsorption alone. Serafin and Friend (26) studied pyridine reactivity on Mo (110) and found that the decomposition of pyridine on H_2 preadsorbed surface occurs at temperatures lower than those on the clean surface. We propose that the activated hydrogen may react with the adsorbed thiophene and facilitates the decomposition and reaction of adsorbed thiophene, which leads to the surface sulfidation of the nitride catalyst easily. This can be further demonstrated by the spectra in Figs. 8 and 9 as discussed in the next part.

Sulfur Effect on Mo_2N/γ-Al_2O_3

As mentioned in the Introduction, the changes of adsorption sites on the surface of nitride catalysts can be monitored according to the stretching frequency of adsorbed CO. For Mo_2N/γ-Al_2O_3, its surface sulfidation can also be probed using CO adsorption because both bands of adsorbed CO on the N sites and Mo sites are sensitive to the surface changes. As discussed above, thiophene adsorbed on Mo_2N/γ-Al_2O_3 does not sulfide the nitride catalyst at temperatures below 673 K. The gradual sulfidation of the Mo_2N/γ-Al_2O_3 surface with the treatment of thiophene/H_2 mixture (Fig. 7) should be due to the decomposition or hydrodesulfurization of thiophene which takes place on Mo_2N/γ-Al_2O_3 at temperatures as low as 373 K. A significant change in the surface property in the course of change from nitride to sulfide occurs at temperatures above 573 K, which is about the temperature for initializing the hydrotreating reactions.

Obviously, thiophene is decomposed or hydrodesulfurized in the presence of H_2 on Mo_2N/γ-Al_2O_3 catalyst at temperatures even as low as 373 K. The IR spectra presented in Fig. 8 clearly show that one or more hydrogenated species, exhibiting IR bands in the region 2870–2970 cm^{-1}, are produced originally on the nitride catalyst when it is exposed to a mixture of thiophene/H_2 at 373 K. The hydrogenated species remain adsorbed on the catalyst surface (see Fig. 8g) under evacuation. They are formed from the reaction of thiophene with the Mo_2N/γ-Al_2O_3 catalyst even at 373 K in the presence of H_2. The 2640-cm^{-1} band due to an S–H stretching vibration observed by Tarbuck *et al.* (24) is absent in our case. This is possibly because the sulfur species produced from the decomposition or desulfurization of thiophene have reacted with the Mo_2N/γ-Al_2O_3 catalyst, leading to the sulfiding of the catalyst surface.

Interestingly, when thiophene contacted with the nitrided catalyst in the absence of H_2 even at 673 K (shown in Fig. 9), no IR bands in the 3000–2800-cm^{-1} region are observed. But in Fig. 5e, a weak band at 2105 cm^{-1} is observed. It is deduced that a small portion of adsorbed thiophene is decomposed at 673 K. The absence of IR bands in the 3000–2800-cm^{-1} region in Fig. 9 is assumed to indicate that a very small amount of decomposed species is produced from adsorbed thiophene. Anyway, the results suggest that thiophene is not reactive to the Mo_2N/γ-Al_2O_3 catalyst without H_2 at temperatures below 673 K. This again indicates that H_2 facilitates the decomposition or hydrodesulfurization of thiophene on the Mo_2N/γ-Al_2O_3 catalyst.

For both nitrided and reduced passivated Mo_2N/γ-Al_2O_3 catalysts, the surface sulfidation is more evident for a surface treated with an H_2S/H_2 mixture than for one treated with the thiophene/H_2 mixture. This indicates that H_2S interacts more strongly than thiophene with Mo_2N/γ-Al_2O_3 catalysts. This is clearly observed from the IR spectra shown in Fig. 3 and the differences between Figs. 7 and 10. In Fig. 3, a small band at 2105 cm^{-1} appears when CO is coadsorbed with H_2S. This suggests that Mo_2N/γ-Al_2O_3 catalyst can be sulfided slightly even at RT. The 2240-cm^{-1} bands become more evident when CO is coadsorbed with H_2S. A similar band at ca. 2230 cm^{-1} was also observed in our previous study (20) when the adsorbed CO on fresh Mo nitride catalyst was outgassed at 573 K. In this study, the formation of the band at 2240 cm^{-1} is possibly due to the adsorbed species formed via the CO adsorption or reaction on the partially sulfided Mo_2N/γ-Al_2O_3 catalyst. According to its high frequency for adsorbed CO, this band can be tentatively assigned to one or several of the following possible species: (1) NCO species, (2) Mo–NC (or Mo–CN) species, (3) Al–NC (or Al–CN) species, or (4) Al–NCO species (27–29). Further experiments are needed to verify its assignment.

The strong interaction between H_2S and the catalyst surface can be also found by comparing the IR spectra presented in Figs. 7 and 10. It can be seen that the critical changes in the surface properties of both nitrided and reduced passivated Mo_2N/γ-Al_2O_3 catalysts take place at temperatures above 373 K when the surface is treated with an H_2S/H_2 mixture, much lower than the temperature for the thiophene/H_2 mixture. It could be deduced that adsorbed thiophene on Mo_2N/γ-Al_2O_3 is first hydrogenated in the presence of H_2 to form adsorbed sulfur species (19), and then the sulfur species participate in the sulfidation of the surface the same as in the case of H_2S.

It is notable that reduced passivated Mo_2N/γ-Al_2O_3 is also sensitive to sulfur species. When coadsorbed with thiophene or H_2S on reduced passivated sample, CO gives no IR bands at all, indicating that the sulfur species adsorb more strongly than CO on the reduced passivated catalyst. When treated with an H_2S/H_2 mixture, the surface of reduced passivated sample seems to be sulfided more easily than that of the nitrided sample. But this difference is slight and is not pronounced as reported in the literature (17, 19). Nagai and co-workers (19) compared the deactivation and sulfidation of Mo/γ-Al_2O_3 catalysts nitrided at different temperatures during the HDS of dibenzothiophene. Their XPS data indicate that the catalyst nitrided at 773 K containing more oxygen is more easily poisoned by sulfur than the well-nitrided sample (containing rare oxygen).

CO adsorption on reduced passivated Mo_2N/γ-Al_2O_3 indicates that most surface Mo sites on the reduced passivated sample are still in a high valence state (Mo^{4+}), namely, the surface oxygen atoms are not completely removed. The study of Nagai *et al.* (19) suggests that the sulfur atoms removed from dibenzothiophene at the initial stage were exchanged not with nitrogen but with oxygen atoms in the molybdenum oxide for the catalyst nitrided at 773 K. It means that oxygen–sulfur exchange is more possible than nitrogen–sulfur exchange. Therefore, for the passivated sample the surface sensitivity to the sulfur effect could be attributed to exchange of sulfur atoms with the surface oxygen that is incorporated during the passivation. Another reason may be that sulfur atoms easily occupy the surface vacancies that are produced by reduction of the passivated Mo_2N/γ-Al_2O_3 catalyst, namely, removal of some of the surface oxygen atoms by H_2. So it seems that the mechanism of sulfidation of reduced passivated Mo_2N/γ-Al_2O_3 catalyst may be different from that of Mo_2N/γ-Al_2O_3 catalyst, especially in the initial stage.

The observed sulfidation of the surface of nitrided and reduced passivated Mo_2N/γ-Al_2O_3 catalysts treated with a thiophene/H_2 or an H_2S/H_2 mixture at HDS temperature is consistent with the thermodynamic calculations by Levy (30) who predicted that nitrides and carbides should be converted to sulfides under sulfiding conditions at high temperature. Our conclusion is also in good agreement with some reported results (1, 9, 13, 22, 31, and 32).

Investigation on the regeneration of the surface of the sulfided catalyst can be helpful for a better understanding of the sulfur effect on the nitride catalysts. The IR results (Fig. 12) show that the surface property of nitride can be partly regained and the sulfur species incorporated into the catalyst surface cannot be fully eliminated by the regeneration with NH_3 at 873 K. This indicates that there are both unexchangeable and exchangeable sulfur species on the surface of the catalyst treated with thiophene/H_2. Higher renitridation temperatures (1123–1173 K) were considered to be favorable for the regeneration of sulfided nitride catalyst (33), while the renitridation after a simple oxidization at 673 K can make the sulfided catalyst be nitrided completely. This means that the sulfur species can be removed thoroughly by the oxidation and the oxide form of molybdenum is then nitrided. It also suggests that oxygen–sulfur exchange is easier than nitrogen–sulfur exchange. These results are in good agreement with the XPS data reported by Nagai *et al.* (19). They also found that there are two kinds of sulfur species on the surface of sulfided molybdenum nitride: sulfide ions (S^{2-}) and disulfide ions (S_2^{2-}) species. Only disulfide ions (S_2^{2-}) can be removed by renitridation with NH_3.

CONCLUSIONS

The influences of both thiophene and H_2S on the surface of the Mo_2N/γ-Al_2O_3 catalyst in the presence or absence of hydrogen have been studied by FT-IR spectroscopy combined with CO adsorption. The IR spectra of adsorbed CO suggest that adsorbed thiophene on Mo_2N/γ-Al_2O_3 keeps its molecular form at temperatures below 673 K. Thiophene can be easily decomposed or hydrodesulfurized in the presence of H_2 on Mo_2N/γ-Al_2O_3 catalyst at temperatures as low as 373 K, at the expense of the sulfidation of the nitride catalyst. The influence of H_2S on Mo_2N/γ-Al_2O_3 catalyst is more evident than that of thiophene and H_2S can sulfide the surface at temperatures above 373 K. The reduced passivated Mo_2N/γ-Al_2O_3 catalyst is also easily sulfided by thiophene or H_2S. The surface of either nitrided or reduced passivated molybdenum nitride is very sensitive to thiophene or H_2S and can be sulfided easily in the presence of H_2. The sulfided surface of Mo_2N/γ-Al_2O_3 catalyst can be partially restored by a renitridation with NH_3 at 873 K, but it can be completely regenerated by a first oxidation and a subsequent renitridation.

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