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On the surface sites of MoP/SiO₂ catalyst under sulfiding conditions: IR spectroscopy and catalytic reactivity studies

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Abstract

The surface sites of MoP/SiO₂ catalysts and their evolution under sulfiding conditions were characterized by IR spectroscopy using CO as the probe molecule. The HDS activities of thiophene were measured on the MoP/SiO₂ catalyst that was subjected to different sulfidation and reactivation pretreatments. Cus $Mo^{\delta+}$ ($0 < \delta \leq 2$) sites are probed on the surface of fresh MoP/SiO₂ by molecularly adsorbed CO, exhibiting a characteristic IR band at 2045 cm⁻¹. The surface of MoP/SiO₂ is gradually sulfided in HDS reactions, as revealed by the shift of the IR band at 2045 to ca. 2100 cm⁻¹. Although the surface of a MoP/SiO₂ catalyst becomes partially sulfided, the HDS activity tests show that MoP/SiO₂ is fairly stable in the initial stage of the HDS reaction, providing further evidence that molybdenum phosphide is a promising catalytic material for industrial HDS reactions. Two kinds of surface sulfur species are formed on the sulfided catalyst: reversibly and irreversibly bonded sulfur species. The MoP/SiO₂ catalyst surface. A detrimental effect of presulfidation on the HDS activity is observed for the MoP/SiO₂ catalyst treated by H₂S/H₂ at temperatures higher than 623 K, which is ascribed to the formation of a large amount of the irreversibly bonded sulfur species. The irreversibly sulfided catalyst can be completely regenerated by an oxidation and a subsequent reduction under mild conditions.

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1. Introduction

In recent decades, there has been worldwide interest in the development of new technologies for the production of clean fuels because of the more stringent environmental legislation and the increase of low-quality stocks. Processes like adsorption, extraction, oxidation, alkylation, and bioprocessing [1] are under exploration. Currently, however, hydroprocessing still appears to be the technologically preferred solution. Other than traditionally used sulfide catalysts, new types of hydroprocessing catalysts that are economic, have a long life, and are highly active are extremely desired. Among the explored catalysts, transition metals modified by main group elements other than sulfur have attracted much attention as they were consid-

* Corresponding author. *E-mail address:* canli@dicp.ac.cn (C. Li). *URL:* http://www.canli.dicp.ac.cn. ered to be potential catalytic materials to substitute for conventional sulfide catalysts. Since the 1980s, transition metal nitride and carbide catalysts have been extensively studied and were found to have superior activities to traditional Mo sulfide catalysts in hydrotreating processes (both hydrodesulfurization (HDS) and hydrodenitrogenation (HDN)) [2–5]. More recently, transition metal phosphides prepared by temperature-programmed reduction (TPR) were reported to have high catalytic activity for both HDN [6–18] and HDS [10–17,19,20]. Among these phosphide catalysts, molybdenum phosphides (MoP, MoP/SiO₂, and MoP/ Al₂O₃) [6–9,14,15,17–19] received the most attention.

Although molybdenum nitrides, carbides, and phosphides show better activities in both HDN and HDS than conventional sulfided Mo catalysts, they behave differently in these hydrotreating reactions. The HDN and HDS activities of Mo nitride and carbide catalysts are initially high but decline with time in the presence of sulfur-containing compounds, which was explained mainly by the irreversible sulfidation of these catalysts [21-23] under reaction conditions. However, it is interesting to note that molybdenum phosphide catalysts show quite stable activities in hydrotreating reactions in the presence of sulfur-containing feedstock, and in some cases even exhibit increased activities with reaction time [7,8,14,15,18,19]. For example, Stinner et al. [7] reported that pure MoP shows a decrease in activity in the presence of H₂S in the HDN of *o*-propylaniline, but the activity increases to a higher level than that at the beginning of the reaction when H₂S is removed. In the hydrotreatment of a model petroleum liquid [14], MoP/Al₂O₃ catalysts showed increased activity in the first several hours in the HDN of quinoline and later reached a stable and higher activity than the commercial NiMoS/Al₂O₃ catalyst without loss of HDS activity. In a study of the HDS of thiophene [19], a MoP/SiO₂ (15 wt% MoP) catalyst was nearly four times more active than a sulfided Mo/SiO₂ catalyst. Interestingly, excluding a decline during the first several hours in the HDS of thiophene, the activity of the MoP/SiO₂ catalyst was found to increase monotonically with time on stream and did not achieve a steady state value even after 150 h [19]. In explanation of the unusual catalytic behaviors of molybdenum phosphide catalysts, these authors assumed the formation of a new type of catalytically active structure of MoP under reaction conditions. But no further experimental evidence was provided. So far, the surface structure and composition of phosphide catalysts under hydrotreating, especially under sulfiding conditions, remain unclear.

It is also notable that the surface sites of molybdenum phosphides were less investigated in contrast with the vast explorations on their reactivities. Although XAFS [14], NMR [15], and XPS [19] studies provided some useful information on the chemical states of P and Mo atoms in molybdenum phosphides, a key question still remains: what are the chemical properties of the surface sites of a nonpassivated or fresh MoP catalyst? Meanwhile, the number of active sites on phosphide catalysts has typically been estimated by CO chemisorption [9,14,15,19]. But little is known about the sites where CO adsorbs on phosphide catalysts.

In this work, the surface sites of a MoP/SiO₂ catalyst were studied by IR spectroscopy using CO as the probe molecule. The HDS activities were measured and compared on fresh, presulfided and reactivated MoP/SiO₂ catalysts. In order to gain insight into the nature of the working surface of phosphide catalysts under HDS conditions, the surface sites of presulfided and reactivated MoP/SiO₂ catalysts were also characterized by CO adsorption. It is shown that a MoP/SiO₂ catalyst is fairly stable in the initial stage of HDS reactions, although IR investigations indicate that the working surface is partially sulfided by adsorbed sulfur species in HDS reactions. The reactivity and spectroscopic results suggest that molybdenum phosphide is potentially a new catalyst for hydrotreating reactions.

2. Experimental

2.1. Catalyst preparation

Unsupported molybdenum phosphide was prepared using the temperature-programmed reduction procedure [6]. Stoichiometric amounts of ammonium heptamolybdate (NH₄)₆-Mo₇O₂₄ · 4H₂O were mixed with diammonium hydrogen phosphate (NH₄)₂HPO₄ in distilled water. A white solid obtained following evaporation of the water was calcined in air at 773 K for 4 h to give a dark blue solid. The calcined solid was subsequently reduced in a temperature-controlled manner from room temperature (RT) to 923 K at a rate of 2 K/min in flowing H₂ (350 ml/min) and kept at 923 K for another 2 h, followed by cooling to RT in H₂. The sample was then passivated at RT in a stream of 1% O₂/N₂ so as to avoid the violent oxidation of the freshly prepared phosphide.

MoP/SiO₂ catalysts were prepared with theoretical Mo loadings of 10, 25, and 35 wt% in order to obtain the model catalyst for practical application. The precursor samples (MoPO_x/SiO₂) were prepared by incipient wetness impregnation of SiO₂ ($S_{BET} = 296 \text{ m}^2/\text{g}$) with an aqueous solution of (NH₄)₆Mo₇O₂₄ · 4H₂O and (NH₄)₂HPO₄. MoP/SiO₂ samples were prepared and passivated using the same procedure applied to pure MoP.

2.2. XRD, BET surface area, and pulsed chemisorption measurements

Crystalline phases of passivated MoP/SiO₂ and MoP samples were detected by X-ray diffraction using the packed powder method, on a Rigaku Rotaflex Ru200B diffractometer with a Cu-K_{α} radiation ($\lambda = 1.5418$ Å).

The experiment of BET surface area was made on an ASAP 2000 system by nitrogen adsorption at 77 K with a static measurement mode. The BET surface areas of the passivated MoP/SiO₂ (10 wt% Mo), MoP, and sulfided Mo/SiO₂ samples were determined to be 236, 10, and 250 m^2/g , respectively.

A CO-pulsed chemisorption experiment was carried out on a ChemBET-3000 instrument. Both reduced and sulfided MoP/SiO₂ (10 wt% Mo) (0.1 g) were subjected to CO titration. The passivated sample was reduced by a flow of H₂ (60 ml/min) from RT to 773 K for 30 min and kept at 773 K for 2 h. The sulfided sample was prepared by sulfiding the reduced MoP/SiO₂ sample at 673 K in a flow of 10% H₂S/H₂ (60 ml/min) for 2 h, the sulfided sample was then reduced by H₂ at 773 K for another 2 h. The sulfided Mo/SiO₂ (10 wt% Mo) sample (0.1 g) was also reduced by a flow of H₂ (60 ml/min) from RT to 773 K for 30 min and kept at 773 K for 2 h. All the samples were purged by He at 280 K for 2 h before the chemisorption of CO at the same temperature.

2.3. HDS activity tests

The catalytic tests for the HDS of thiophene were measured in a continuous microreactor. The liquid samples were analyzed by a gas chromatograph (GC920) equipped with a flame ionization detector (FID) and a 30-m-long capillary column (hp-1). The reaction conditions were set at a total pressure of 3.0 MPa, a liquid (2 wt% thiophene/decahydronaphthalene) flow rate of 6 ml/h, and a hydrogen flow rate of 60 ml/min. The products were analyzed by a gas chromatograph (Agilent GC 6890N) equipped with a FID detector and a 50-m-long capillary column (HP-plot/Al₂O₃ S).

For the sake of comparison, a sample (ca. 0.5 g) of passivated MoP/SiO₂ (10 wt% Mo) catalyst was tested continuously for all the reactions operated under different conditions. The passivated MoP/SiO2 catalyst was activated in situ in the reactor with H₂ (100 ml/min) at 773 K for 2 h and then cooled to reaction temperature. The activated sample was initially tested at 593 K for the HDS of thiophene, then the temperature was increased to 623 and 673 K, and the HDS activity was measured at each temperature. In order to examine the sulfiding effect on MoP/SiO2 catalysts, the catalyst after the continuous reaction was subjected to a flow of 10% H₂S/H₂ (60 ml/min) at different temperatures (593, 623, 673, and 723 K) for 2 h. After sulfidation at each temperature, the HDS test was carried out at 623 K. After a sulfidation at 723 K and the HDS measurement, the catalyst sample was either reduced by H₂ (100 ml/min) at 773 K or oxidized in flowing air (100 ml/min) at 673 K for 2 h and then activated by H₂ (150 ml/min) from RT to 923 K (5 K/min) and kept at 923 K for another 2 h. The reactivated sample was then tested for the HDS of thiophene at 623 K again. Each set of the HDS activity test was maintained for at least 6 h.

A MoO_3/SiO_2 (10 wt% Mo) precursor was sulfided in flowing 10% H_2S/H_2 (60 ml/min) at 673 K for 2 h. The sulfided Mo/SiO₂ sample was then cooled to 623 K and purged by N₂ (60 ml/min) for 20 min before the HDS of thiophene started. The reaction conditions were the same as those for MoP/SiO₂.

2.4. IR studies

An oxide precursor MoPO_x/SiO₂ or a passivated MoP/ SiO₂ (10 wt% Mo) sample was pressed into a self-supporting wafer (ca. 15 mg/cm²) and put into a quartz IR cell with CaF₂ windows to reduce in flowing H₂ at different temperatures (673, 723, 773, 873, and 923 K). The reduced sample was evacuated at 773 K for 60 min and subsequently cooled to RT. Several IR experiments were then performed as follows:

- (1) The sample was exposed to 10 Torr CO (1 Torr = 133.33 Pa) for probing the surface sites.
- (2) The sample was treated by a mixture of thiophene/ H_2 (4/400 Torr), or a mixture of H_2S/H_2 (4/400 Torr) at dif-

ferent temperatures (373, 473, 573, and 673) for 1 h and then the sample was evacuated at 773 K for 20 min. As the sample was cooled to RT, 10 Torr of CO was introduced into the IR cell.

(3) The sample pretreated by a mixture of thiophene/H₂ (4/400 Torr) statically at 673 K or a flow of 10% H₂S/H₂ (60 ml/min) at different temperatures (573 and 773 K) was reactivated by two procedures: a reduction at 773 and 923 K by H₂, or an oxidation by air at 673 K for 2 h and then a reduction at 923 K by H₂. Thus treated sample was also probed by CO adsorption. The flow rate of H₂ in the different treatments was set at 150 ml/min and a heating rate of 5 K/min was used.

All infrared spectra were collected 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 in transmission mode after the sample was outgassed, unless otherwise indicated.

3. Results

3.1. XRD and CO chemisorption

The XRD patterns of SiO₂, MoP, and MoP/SiO₂ with different Mo loadings are shown in Fig. 1. The XRD pattern of bulk MoP (Fig. 1e) gives several peaks at 27.6, 31.8, 42.8, 57.0, 64.6, 67.2, and 74.0°, similar to the standard pattern from the powder diffraction file (PDF) [24] as well as that reported in the literature [6,7,14,15,19]. The diffraction patterns for MoP/SiO₂ samples with 25 and 35 wt% Mo exhibit similar peaks of bulk MoP, confirming the successful preparation of MoP on the silica support. The passivated MoP/SiO₂ sample (10 wt% Mo) only shows the features of amorphous silica (Fig. 1a). The results suggest that MoP par-



Fig. 1. XRD patterns of (a) SiO₂; (b) passivated MoP/SiO₂ (10 wt% Mo); (c) passivated MoP/SiO₂ (25 wt% Mo); (d) passivated MoP/SiO₂ (35 wt% Mo); and (e) passivated MoP.



Fig. 2. IR spectra of CO adsorbed at RT on passivated MoP/SiO₂ catalyst reduced at different temperatures: (a) 673 K; (b) 723 K; (c) 773 K; (d) 873 K; and (e) 923 K.

ticles are well dispersed on the support when the Mo loading is low.

The CO chemisorption capacities of reduced and sulfided MoP/SiO₂ and sulfided Mo/SiO₂ samples are 135.5, 39.6, and 4.2 μ mol/g, respectively. The MoP/SiO₂ samples show much higher chemisorption capacities than the sulfided Mo/SiO₂. A sulfidation of the MoP/SiO₂ sample leads to a great decrease of its chemisorption capacity.

3.2. CO adsorption on MoP/SiO₂

As the freshly prepared molybdenum phosphide will be oxidized when exposed to air, a passivation process is needed in order to avoid the oxidation of the fresh catalyst. Therefore, a passivation layer exists on the passivated sample and investigation on its surface sites is possible only when the passivation layer is removed. Fig. 2 shows the IR spectra of CO adsorbed on passivated MoP/SiO2 reduced by H₂ at different temperatures. No IR band of adsorbed CO can be observed on the sample reduced at 673 K, indicating that the passivation layer was not reduced and the passivated MoP/SiO₂ does not adsorb CO. Great changes of the spectra take place for the sample reduced at 723 K: a main band at 2050 cm^{-1} appears with a shoulder at 2075 cm^{-1} . The shoulder band at 2075 cm^{-1} disappears with further elevation of the reduction temperatures while the band at 2050 cm^{-1} increases gradually in intensity, indicating that more surface sites for CO adsorption are generated owing to the deeper reduction. The 2050-cm⁻¹ band slightly shifts to 2045 $\rm cm^{-1}$ and becomes predominant for the sample reduced at 923 K.

CO adsorption on the oxidized precursor ($MoPO_x/SiO_2$) sample reduced at different temperatures was also conducted similarly to that on passivated MoP/SiO₂. Identical IR spec-



Fig. 3. IR spectra of CO adsorbed at RT on MoP/SiO₂ catalyst as a function of pressure and temperature: (a) 10 Torr at RT; (b) evacuated to 10^{-4} Torr at RT; (c) evacuated to 323 K; (d) evacuated to 423 K; and (e) 10 Torr CO was readsorbed on the sample and a brief outgas at RT.

tra were obtained for adsorbed CO on the two types of samples, indicating that H₂ reactivation of the passivated phosphide results in negligible change of the surface nature. According to the preparation process, the passivated MoP/SiO₂ sample reduced at 923 K can be regarded as fresh molybde-num phosphide on silica. Therefore, adsorbed CO on fresh MoP/SiO₂ exhibits a characteristic band at 2045 cm⁻¹ that can be due to adsorbed CO on Mo sites [23–29] on the surface of MoP. The fresh sample is denoted as MoP/SiO₂ on which following experiments will be carried out.

Fig. 3 presents the IR spectra of CO adsorbed on MoP/SiO₂ as a function of pressure and temperature, which reflects the stability of the adsorbed CO. The characteristic band at 2045 cm⁻¹ persists under vacuum at RT, indicating that the adsorbed CO is rather stable. The band at 2045 shifts to 2022 cm⁻¹ with decreased intensity when the sample was evacuated at 323 K (Fig. 3c). A further evacuation at 423 K leads to a dramatic decrease in intensity of the IR band for adsorbed CO which is observed at 2015 cm⁻¹ (Fig. 3d). After a complete removal of adsorbed CO, CO was introduced again to the MoP/SiO₂ sample and the corresponding IR spectrum (Fig. 3e) is very similar to Fig. 3a, implying that CO is reversibly adsorbed on molybdenum phosphide.

IR spectra in the OH-stretching region were also recorded for passivated MoP/SiO₂ reduced at different temperatures and shown in Fig. 4b–4f. Two IR bands at 3745 and 3665 cm⁻¹ can be distinguished in the ν (OH) region for the samples reduced below 923 K (Fig. 4b–4e) and the band at 3665 cm⁻¹ decreases in intensity with the elevated reduction temperatures. As the temperature reaches to 923 K, only the band at 3745 cm⁻¹ can be observed. The band at 3745 cm⁻¹ obviously originated from the stretching of Si– OH as revealed by the ν (OH) region of a pure SiO₂ sample



Fig. 4. IR spectra in the ν (OH) region for (a) SiO₂; and passivated MoP/SiO₂ catalyst reduced at (b) 673 K; (c) 723 K; (d) 773 K; (e) 873 K; (f) 923 K; (g) P/SiO₂; and (h) exposure to 15 Torr air after (f).

outgassed at 773 K (Fig. 4a). The band at 3665 cm⁻¹ is possibly due to ν (P–OH) according to the study of phosphate on γ -Al₂O₃ where an IR band at 3680 cm⁻¹ was detected and assigned to a P–OH group of supported phosphate [30]. This assignment is supported by the IR spectrum (Fig. 4g) of a P/SiO₂ sample that was prepared by impregnation of (NH₄)₂HPO₄ on SiO₂. Two sharp bands are observed at 3775 and 3665 cm⁻¹ in the OH-stretching region when this sample was reduced at 923 K and outgassed at 773 K. So the band at 3665 cm⁻¹ can be attributed to ν (P–OH) of phosphate species on the surface of MoP/SiO₂. The decrease in intensity of the 3665-cm⁻¹ band indicates the gradual reduction of the surface phosphate species by H₂.

The surface phosphate species of MoP/SiO₂ is possibly formed by the oxidation of surface P atoms during the passivation process. With an attempt to work out the passivation effect, the MoP/SiO₂ sample reduced at 923 K was exposed to 15 Torr air and the corresponding IR spectrum was collected and shown in Fig. 4h. The band at 3665 cm⁻¹ due to ν (P–OH) appears again, indicating that part of the surface P atoms is transformed to phosphate species upon oxidation. Thus, it is deduced that the role of passivation is partly to produce a protection layer of phosphate on the surface of MoP/SiO₂.

3.3. Catalytic performance of HDS

To be a potential catalyst for hydrotreating processes, it is crucial that the catalyst remains stable under sulfurcontaining conditions. In order to investigate the stability of MoP under HDS conditions and its tolerance to sulfur, the MoP/SiO₂ catalyst was tested for the HDS of thiophene under various conditions and the HDS activities are compared in Fig. 5A. When the reaction temperature is set at 593 K



Fig. 5. (A) A comparison of the thiophene HDS activities of fresh, sulfided, and reactivated MoP/SiO₂ catalysts: (a) fresh catalyst at reaction temperature of 593 K; (b) at reaction temperature of 623 K after (a); (c) at reaction temperature of 673 K after (b); (d) the catalyst after (c) was sulfided by H_2S/H_2 at 593 K; (e) the catalyst after (d) was sulfided by H_2S/H_2 at 623 K; (f) the catalyst after (e) was sulfided by H_2S/H_2 at 673 K; (g) the catalyst after (f) was sulfided by H_2S/H_2 at 723 K; (h) the catalyst after (g) was reduced by H_2 at 773 K; (i) the catalyst after (h) was first oxidized by air at 673 K and then reduced by H_2 at 923 K. The reaction temperature for (d)–(j) was all set at 623 K. (B) Production distributions of MoP/SiO₂ and sulfided Mo/SiO₂ catalysts for thiophene HDS at 623 K after 6 h on stream.

(Fig. 5A-a), the HDS activity increases with reaction time following an initial decline. The conversion of thiophene exceeds 60% at 6 h on stream. As the reaction temperature increases to 623 and 673 K, the corresponding conversion of thiophene improves to a higher level, which is obviously due to the temperature effect on the reaction rate. It is interesting to observe that the HDS activity of a MoP/SiO₂ catalyst goes up gradually over time in the initial stage in the temperature

range 593–673 K. The activity trend exhibited by MoP/SiO₂ catalyst implies that the surface of MoP/SiO₂ may undergo some changes under HDS conditions.

To check further how MoP behaves under sulfiding conditions, more severe sulfiding conditions were used; i.e., H₂S/H₂ was used to sulfide the MoP/SiO₂ catalyst at different temperatures. After each sulfidation treatment, HDS activity on the sulfided catalyst was measured at 623 K and shown in Fig. 5A-d-5A-f. For the catalyst sulfided at 593 and 623 K (Fig. 5A-d and 5A-e), the conversion of thiophene is at level similar to that in Fig. 5A-b. When the sulfidation pretreatment was conducted at higher temperatures (673 and 723 K), a detrimental effect on the HDS activity is evidenced by the continuous drop of the conversion of thiophene (Fig. 5A-f and 5A-g), which is much lower than that in Fig. 5A-b. This is probably due to the modification of the phosphide surface by sulfur species. A reduction of the MoP/SiO₂ catalyst after Fig. 5A-g by H₂ at 773 K does not show an apparent positive effect on the HDS activity as shown in Fig. 5A-h. When the catalyst was reactivated by an oxidation at 673 K and a subsequent reduction at 923 K (Fig. 5A-i), the conversion of thiophene rises to around 80%, in a level similar to that of a freshly activated MoP/SiO₂ catalyst (Fig. 5A-b). This indicates that the partly deactivated catalyst may have been resumed to molybdenum phosphide after the reactivation treatment.

For a comparison, the activity of sulfided Mo/SiO₂ for thiophene HDS was also tested at 623 K and shown in Fig. 5A-j. The HDS activity decreases with time on stream, different from the trend shown by MoP/SiO₂ (Fig. 5A-b). The HDS activities of thiophene after 6 h on stream are presented in terms of areal rate and turnover frequency (TOF) in Table 1 for both MoP/SiO2 and sulfided Mo/SiO2 catalysts. The TOFs were calculated using CO chemisorption capacities of reduced and sulfided MoP/SiO₂, and sulfided Mo/SiO₂ as a measurement of active sites of the three catalysts. The stoichiometry of a CO/active site is assumed to be 1 for the three catalysts. The areal rates for MoP/SiO₂ and sulfided Mo/SiO₂ are nearly equal, but the turnover frequencies of both reduced and sulfided MoP/SiO2 are much smaller than that of sulfided Mo/SiO₂. These HDS rates were substantially lower than those reported in the literature [19]. The reason could be that the HDS reaction was carried out under atmospheric pressure and the HDS activities were measured after 150 h on stream in Ref. [19], while our results were obtained after 6 h on stream and the reaction was operated at high pressure. But it is interesting to note

Table 1

HDS activities of thiophene after 6 h on stream

	Areal rate	TOF $(\times 10^{-3} \text{ s}^{-1})^*$	
	(nmol of thiophene/m ² of cat/s)	Reduced	Sulfided
MoP/SiO ₂	2.43	4.2	14.5
Sulfided Mo/SiO2	2.48	-	147.9

* Stoichiometry of CO/active site is assumed to be 1 for all samples.

that the initial activity trends shown by MoP/SiO₂ and sulfided Mo/SiO₂ in Ref. [19] are very similar to those observed in this study; i.e., MoP/SiO₂ has a lower HDS activity than sulfided Mo/SiO₂ at the initial reaction stage, but with time on stream, the two catalysts show inverse trends in activities and MoP/SiO₂ becomes more active than sulfided Mo/SiO₂. So it may be expected that the thiophene HDS activity of MoP/SiO₂ would also exceed that of sulfided Mo/SiO₂ with time on stream under the reaction conditions employed in this study. Running the reaction for longer time (up to hundreds of hours) is, however, beyond the main topic of this study. Detailed HDS reactivity studies of MoP catalysts are underway in this laboratory.

Fig. 5B shows the product distributions of MoP/SiO₂ and sulfided Mo/SiO₂ catalysts for thiophene HDS at 623 K after 6 h on stream. The selectivities to butanes, 1-butene, and 2-butenes do not show obvious differences for both catalysts, indicating that the surface of a MoP/SiO₂ catalyst may resemble that of sulfided Mo/SiO₂ to some extent under HDS conditions. The major products are butanes for both MoP/SiO₂ and sulfided Mo/SiO₂ catalysts. This is different from the product distribution on the two catalysts in Ref. [19] where butenes are the major products. An explanation could be the big differences in the reaction pressures employed in Ref. [19] and this study.

3.4. CO adsorption on MoP/SiO₂ pretreated with thiophene/ H_2 or H_2S/H_2

Since molybdenum phosphide catalysts exhibit a unique catalytic behavior in HDS reactions as shown by the above results and the literature [7,19], it is desirable to gain information on the surface properties of the working catalysts. IR spectroscopy combined with CO as probe molecule is a suitable technique to this goal. Thiophene/H₂ and H₂S/H₂ were selected to study their influences on the surface property of MoP/SiO₂ catalysts under conditions similar to those used in Fig. 5.

Fig. 6 exhibits the IR spectra of CO adsorbed on MoP/ SiO₂ treated with a thiophene/H₂ (4/400 Torr) mixture at different temperatures. The band at 2045 cm⁻¹ shifts to higher frequencies when the treatment temperature is increased, e.g., to 2047 cm^{-1} at 373 K, to 2049 cm^{-1} at 473 K, to 2055 cm^{-1} with a shoulder at 2090 cm⁻¹ at 573 K, and to 2100 cm⁻¹ at 673 K. Meanwhile, a shoulder at ca. 2055 cm^{-1} can still be distinguished for the sample treated at 673 K. The appearance of the band at 2100 cm^{-1} indicates the sulfidation of the phosphide 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 [21,23,27]. The results show that the surface of the MoP/SiO₂ catalyst is partially sulfided when treated with the thiophene/ H_2 mixture at 673 K. A separate detection of the changes of thiophene itself during the treatments at different temperatures shows that thiophene becomes reactive with hydrogen on the MoP/SiO₂ catalyst at and above 373 K.



Fig. 6. IR spectra of CO adsorbed at RT on (a) MoP/SiO₂ catalyst; (b) on the same catalyst after it was treated with a thiophene/H₂ (4/400 Torr) mixture at 373 K; (c) 473 K; (d) 573 K; and (e) 673 K for 1 h.



Fig. 7. IR spectra of CO adsorbed at RT on (a) MoP/SiO₂ catalyst; (b) on the same catalyst after it was treated with H_2S/H_2 (4/400 Torr) at RT; (c) 373 K; (d) 473 K; (e) 573 K; and (f) 673 K for 1 h.

Thus, the gradual sulfidation of MoP/SiO₂ catalysts can be ascribed to the HDS of thiophene [31-34].

Fig. 7 shows the effect of H_2S/H_2 treatment on the surface property of MoP/SiO₂ probed by CO adsorption. When the sample was treated by H_2S/H_2 at RT (ca. 298 K) for 1 h, adsorbed CO gives a sharp band at 2100 cm⁻¹ with a shoulder at 2078 cm⁻¹, indicating a partial sulfidation of the catalyst surface. As the pretreatment temperature increases to 473 K, the shoulder band at 2078 cm⁻¹ disappears while the band at 2100 shifts to 2102 cm⁻¹ and becomes dominant. A further increase to 673 K only leads to a slight shift of the band at 2102 to 2104 cm⁻¹. It is apparent that H_2S/H_2 can sulfide



Fig. 8. IR spectra of CO adsorbed at RT on (a) MoP/SiO₂ catalyst; (b) on the same catalyst after it was treated with thiophene/H₂ (4/400 Torr) at 673 K for 4 h; (c) on the thiophene-sulfided MoP/SiO₂ catalyst after a reduction by H₂ at 923 K; and (d) on the sulfided MoP/SiO₂ catalyst after it was regenerated by oxidation at 673 K and then reduction at 923 K.

the surface of molybdenum phosphide catalysts much easier than thiophene/ H_2 does.

3.5. CO adsorption on reactivated MoP/SiO₂ pretreated by thiophene/H₂ or H₂S/H₂

IR investigation on the reactivation of the sulfided MoP/ SiO₂ catalyst can be helpful for a better understanding of the surface composition and structure of MoP/SiO2 catalysts under sulfiding conditions, which would provide a possible explanation for the activity results. Similar presulfidation and reactivation conditions in Fig. 5 were also used in the IR studies. After being pretreated by a mixture of thiophene/ H_2 at 673 K for 4 h, the MoP/SiO₂ sample was reactivated in two different ways: a H₂ reduction at 923 K or an oxidation by air at 673 K and then a reduction at 923 K by H₂. IR spectra of CO adsorbed on thus treated samples are shown in Fig. 8. Adsorbed CO on fresh MoP/SiO2 gives a characteristic band at 2045 cm⁻¹, as presented in Fig. 8a. After the sample was treated with thiophene/H₂ at 673 K for 4 h, CO adsorption shows one band at 2100 cm^{-1} with a weak shoulder at 2055 cm^{-1} (Fig. 8b). This is nearly identical to the spectrum of CO on the MoP/SiO2 catalyst pretreated by thiophene/H₂ at 673 K for 1 h (Fig. 6e), suggesting that further sulfidation of MoP/SiO₂ catalyst is limited at 673 K under HDS conditions. A H2 reduction of the partially sulfided sample leads to a great change of the IR spectrum for adsorbed CO. The band at 2100 shifts to 2092 cm⁻¹ and becomes a shoulder, while a main band at 2052 cm^{-1} appears, indicating that the catalyst surface is dominated by molybdenum phosphide. As the partially sulfided sample was oxidized prior to reduction, adsorbed CO exhibits a strong band at 2045 cm⁻¹ again, which implies that the partially sulfided MoP/SiO₂ catalyst is fully recovered to phosphide nature. The total recovery of the sulfided catalyst suggests that most P atoms in MoP are not removed or exchanged by sulfur species derived from the HDS of thiophene.



Fig. 9. (A) IR spectra of CO adsorbed at RT on (a) MoP/SiO₂ catalyst; (b) on the same catalyst after it was treated with a flow of 10% H_2S/H_2 at 573 K for 2 h; (c) on the sulfided MoP/SiO₂ catalyst after a reduction by H₂ at 773 K; (d) on the sulfided MoP/SiO₂ catalyst after a reduction by H₂ at 923 K; and (e) on the sulfided MoP/SiO₂ catalyst after it was regenerated by oxidation at 673 K and then reduction at 923 K. (B) IR spectra of CO adsorbed at RT on (a) MoP/SiO₂ catalyst; (b) on the same catalyst after it was treated with a flow of 10% H₂S/H₂ at 773 K for 2 h; (c) on the sulfided MoP/SiO₂ catalyst after a reduction by H₂ at 923 K; (d) on the sulfided MoP/SiO₂ catalyst after a reduction by H₂ at 923 K; and (e) on the sulfided MoP/SiO₂ catalyst after it was regenerated by oxidation at 673 K and then reduction at 923 K.

In order to find out how resistant molybdenum phosphide is to sulfur treatment, more severe sulfiding conditions were employed. Since MoP/SiO₂ catalysts can be sulfided facilely by the mixture of H₂S/H₂ as revealed by Fig. 7, a MoP/SiO₂ sample was subjected to flowing H_2S/H_2 (10% H_2S) at different temperatures (573 and 773 K) for 2 h. This sulfidation treatment is similar to that employed in the reactivity tests (Fig. 5A-d and 5A-g). The MoP/SiO₂ catalysts sulfided at 573 and 773 K were denoted as a 573 K-sulfided and 773 K-sulfided sample, respectively. The sulfided samples were also reactivated by the above-used methods and the corresponding IR spectra of adsorbed CO are presented in Fig. 9A (573 K-sulfided) and Fig. 9B (773 K-sulfided). Adsorbed CO on the samples sulfided at 573 and 773 K, respectively, give a sharp band at 2103 and 2105 cm^{-1} , suggesting a full sulfidation of the surface of MoP/SiO₂. When the 573 K-sulfided sample was activated by H₂ at 773 K, adsorbed CO gives a main band at 2100 cm^{-1} with a shoulder at 2070 cm⁻¹ (Fig. 9A-c). While for the 773 Ksulfided sample, the IR band for adsorbed CO slightly shifts to 2101 cm^{-1} and the bandwidth becomes a little broader (Fig. 9B-c), revealing a negligible change of the surface states of the sulfided sample. As the H2-reduction temperature is increased to 923 K, the main band goes to 2060 cm^{-1} while a shoulder at 2092 cm^{-1} is still evident (Fig. 9Ad), indicating that the phosphide is dominant on the reactivated sample catalyst. For the 773 K-sulfided sample, the band at 2101 shifts to 2095 cm⁻¹, meanwhile a shoulder at 2067 cm^{-1} is observed, implying that the catalyst surface is still mainly in sulfide form. An oxidation and a subsequent reduction completely recover the phosphide nature of both sulfided catalysts as evidenced by the appearance of the characteristic IR band of adsorbed CO at 2045 cm⁻¹ in Figs. 9A-e and 9B-e. This also indicates that P atoms in MoP/SiO₂ are resistant to sulfur species at temperatures even as high as 773 K, namely, MoP/SiO₂ catalyst is fairly stable under sulfur-containing circumstances.

4. Discussion

4.1. Surface sites of MoP/SiO₂

A characteristic IR band at 2045 cm⁻¹ is observed for adsorbed CO on MoP/SiO₂ (Figs. 2 and 3). The assignment of this IR band can be well aided by a number of related studies of CO adsorption on Mo-based catalysts [23–29]. Decanio and Storm [35] investigated the adsorption of CO on mildly reduced Mo/Al₂O₃ catalysts with different Mo loadings. Adsorbed CO on a 12 wt% Mo/Al₂O₃ catalyst reduced at 703 K shows three bands at 2175, 2050, and 2130 cm⁻¹, attributed to cus Mo⁴⁺, Mo²⁺ sites, and physisorbed CO, respectively. In an IR study of CO adsorption on sulfided Mo/Al₂O₃ catalysts at 77 K, Müller et al. [27] assigned the intense band at 2110 cm⁻¹ to CO adsorbed on cus Mo²⁺ located on edge planes of MoS₂, and the weak band at 2060 cm⁻¹ to CO

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bonded to cus Mo²⁺ located on the corners of MoS₂. Bussell and co-workers [23] investigated the surface sites of reduced passivated Mo₂N/Al₂O₃ and Mo₂C/Al₂O₃ catalysts using IR spectroscopy. Except for the main band at 2178 cm^{-1} due to CO on oxidized Mo sites that were produced during the passivation process, a shoulder band was observed at 2060 cm^{-1} and was attributed to CO adsorbed on cus Mo²⁺ sites, i.e., carbided Mo. In a comparative IR study of the surface sites of passivated and fresh Mo₂N/Al₂O₃ catalysts by CO probing, a main band at 2179 cm^{-1} (CO on Mo⁴⁺) and two weak bands at 2102 (CO on Mo^{$\delta+$} (2 < δ < 4)) and 2035 cm^{-1} (CO on Mo^{δ +} (0 < δ < 2)) were observed on the reduced passivated catalyst, while a characteristic IR band at 2045 cm⁻¹ (CO on Mo^{δ +} (0 < δ < 2)) was detected on the fresh catalyst [27,28]. The totally different IR spectral features suggest the different surface sites of the two kinds of catalysts.

On the basis of the survey from the above-noted studies and other reports in the literature [23–29,35–38], a general assignment of CO adsorption on Mo sites can be drawn as follows. Linearly carbonyl species bonded to cus $Mo^{\delta+}$ $(3 < \delta < 5)$ show ν (CO) frequencies higher than that of free CO molecule (2143 cm⁻¹). On the contrary, ν (CO) frequencies lower than 2143 cm⁻¹ originate from adsorbed CO on cus Mo^{δ +} (0 < δ < 3) sites. Adsorbed CO on cus Mo²⁺ sites gives an IR band in the range 2040–2070 cm^{-1} . Therefore, the IR band at 2045 cm⁻¹ for CO adsorbed on MoP/SiO₂ can be attributed to linearly bonded CO on the cus $Mo^{\delta+}$ $(0 < \delta \leq 2)$ sites of MoP/SiO₂ catalyst. Although metal phosphides are considered to have a metallic nature [39], CO adsorption indicates that the Mo atoms in molybdenum phosphide are positively charged due to the charge transfer from Mo to the electronegative P atoms. The XPS study of molybdenum phosphides [19] showed a binding energy of 228.4 eV for phosphided Mo. Considering the electron transfer from Mo to P in MoP and MoP/SiO₂, the authors assigned this binding energy to a Mo^{$\delta+$} (0 < $\delta \leq 4$) species. This is consistent with our IR results about the valence state of Mo sites of MoP/SiO2 catalyst.

IR results in Fig. 3 show that CO is strongly and reversibly adsorbed on fresh MoP/SiO₂ catalysts. This is different from CO on fully reduced Mo catalysts on which most CO is disassociatively absorbed and the rest CO is weakly bonded and can be removed by prolonged evacuation at RT [25,26]. It is suggested that the adsorption behavior of CO on the surface Mo of fresh molybdenum phosphide is greatly modified by the presence of P atoms, which distinguishes the surface properties of molybdenum phosphide from those of metallic molybdenum and molybdenum oxides. This is also found in the cases of molybdenum nitride [28,29] and carbide [40].

The disappearance of the IR band at 3665 cm⁻¹ due to ν (P–OH) (Fig. 4f) suggests that the surface oxygen atoms have been eliminated by H₂ and thus the phosphorous atoms are in a reduced state. Namely, the passivation layer on MoP/SiO₂ has been completely removed. A recent time-resolved XRD study on the preparation of MoP and MoP/SiO₂ from oxide precursors suggested that the reduction of phosphate-type species (PO_x) is the final and determining step in the formation of MoP [20]. The ³¹P MAS NMR results of MoP/SiO₂ [18] also indicated that surface phosphate species are formed upon passivation of a fresh MoP/SiO₂ sample and can be removed by a H₂ reduction at 673 K. Therefore, we can deduce that the passivated sample reduced above 873 K can be regarded as fresh MoP/SiO₂, consistent with the results from CO adsorption (Fig. 2). It can also be inferred from Figs. 2 and 4 that the surface Mo and P sites of a fresh MoP/SiO₂ catalyst are in highly reduced state. To our knowledge, this is the first IR report of the nature of the surface sites of a fresh MoP/SiO₂ catalyst in the literature.

It is interesting to note that the passivated molybdenum phosphide can be activated to a fresh one by H₂ at temperatures above 873 K, indicating that oxygen atoms in the passivation layer can be completely removed by H₂ treatment. Even when the reduction temperature is higher than 723 K, Mo sites on MoP/SiO₂ catalysts are activated to a low valence state. This is quite different from the cases of passivated molybdenum nitride and carbide catalysts [23,29]. The IR results of CO adsorption on Mo₂N/Al₂O₃ and Mo₂C/Al₂O₃ catalysts activated by H₂ at 750 K showed the predominance of oxidized Mo sites (Mo⁴⁺) on the catalysts surface [23]. Even when the Mo₂N/Al₂O₃ catalyst was reduced by H₂ at 873 K, Mo⁴⁺ species still dominate on the nitride surface [29]. So it was concluded that a certain amount of oxygen incorporated into the passivated Mo nitride and carbide particles during the passivation process cannot be removed by an H2 reduction. Namely, the working surfaces of H₂-activated molybdenum nitride and carbide catalysts are actually in a oxynitride or oxycarbide form. A complete removal of the incorporated oxygen needs a renitridation of the passivated nitride catalyst by ammonia [29]. On the contrary, our IR results here suggest that the passivated molybdenum phosphides can be readily activated by H₂ to fresh phosphides and Mo^{δ +} (0 < $\delta \leq 2$) sites dominate on the surface of molybdenum phosphide reduced by H₂ above 623 K. The support may play an important role because Mo can be more easily reduced on SiO2 than on Al_2O_3 .

The low valence state of Mo sites is of significance to hydrotreating reactions as inferred from the study of HDS of dibenzothiophene on nitrided catalysts [41]. On investigation of the HDS of dibenzothiophene on Mo/ γ -Al₂O₃ catalysts nitrided at different temperatures, Nagai et al. [41] found that the distribution of Mo oxidation states of the nitrided Mo/ γ -Al₂O₃ catalysts is related to the HDS activity and that metallic Mo and Mo²⁺ are the most active species for the HDS of dibenzothiophene. Therefore, the differences in the surface states could be one of the reasons that molybdenum phosphides exhibit better catalytic activities in hydrotreating reactions than the corresponding nitride and carbide catalysts.

4.2. Evolution of the surface sites of MoP/SiO₂ under sulfiding conditions

The HDS activity test (Fig. 5A-a–5A-c) reveals that MoP/SiO_2 shows stable activity over reaction time in the initial stage of the HDS reaction. This unique catalytic behavior of the MoP/SiO₂ catalyst distinguishes it from Mo nitride and carbide catalysts. For Mo₂N and Mo₂C catalysts, they were found to show either decreased activity during the whole HDS reaction or stable activity after decreasing in the initial reaction stage [3,23]. The unusual activity trend shown by MoP/SiO₂ can be well correlated to the IR investigations on the nature of the surface sites of MoP/SiO₂ that was treated by thiophene/H₂ and H₂S/H₂ under conditions similar to those in thiophene HDS reactions.

As presented in Fig. 6, the spectra of adsorbed CO on MoP/SiO₂ catalysts treated with thiophene/H₂ clearly show that the catalyst surface is gradually sulfided with the elevated treatment temperatures. This is in good accordance with the observation of the increasing reactivity of thiophene on the phosphide catalyst in the presence of H₂ at elevated temperatures. When the sample is treated with thiophene/H₂ at 673 K, the band at 2045 shifts to 2096 cm^{-1} , but a weak shoulder at 2055 cm⁻¹ is still present, suggesting a partial sulfidation of the surface of the MoP/SiO₂ catalyst. In the case of H₂S, the surface of the MoP/SiO₂ catalyst is sulfided at treatment temperatures above 373 K (see Fig. 7). This is understandable as the sulfiding effect of H_2S is more severe than thiophene, which was also observed on Mo₂N/Al₂O₃ catalysts [21]. Therefore, it can be reasonably deduced that the surface of a MoP/SiO₂ catalyst would be partially sulfided under HDS conditions. Then it is easy to understand that the product distributions of MoP/SiO₂ and sulfided Mo/SiO₂ catalysts for thiophene HDS are close (Fig. 5B). Thus, for activity evaluation of molybdenum phosphide catalyst, the measurement of the number of surface sites by CO chemisorption should be conducted on a MoP/SiO₂ catalyst that is sulfided under conditions identical to those of the HDS reaction. However, the turnover frequency listed in Table 1 of sulfided MoP/SiO₂ catalysts for thiophene HDS is still much smaller than that of sulfided Mo/SiO₂, indicating that the surface states are not identical for MoP/SiO2 and sulfided Mo/SiO2 after 6 h on stream. And it should be noted that the activity trends shown by the two catalysts are quite different. The HDS activity increases with time on stream for MoP/SiO2 while it declines for sulfided Mo/SiO₂ within 6 h on stream. If the reaction time is extended, assuming a similar trends as shown in the literature [19], thiophene HDS activity for MoP/SiO₂ would continuously increase with time on stream while it gradually decrease for sulfided Mo/SiO2. Therefore, the surface of MoP/SiO₂ evolves into a more active form with time on stream under a HDS reaction [19]. The evolved surface sites may show some differences from those of sulfided Mo/SiO₂ and this is supported by our IR results.

The presence of the shoulder band at ca. 2055 cm^{-1} for adsorbed CO on MoP/SiO2 catalyst pretreated by thiophene/ H₂ at 673 K (Figs. 6e and 8b) suggests that the surface of the MoP/SiO₂ catalyst is only partially sulfided under HDS conditions. Both P and S may coexist with Mo on the surface of the partially sulfided catalyst. This is also supported by the IR study of the reactivation of the thiophene-sulfided MoP/SiO₂ catalyst (Fig. 8), which helps us to gain further insight into the surface composition of the working catalyst. A H₂ reduction of the sulfided MoP/SiO₂ partially restores the phosphide nature of the catalyst as evidenced by the appearance of the IR band at ca. 2055 cm^{-1} . The sulfided catalyst is completely recovered to a phosphide nature after an oxidation and a subsequent reduction. It implies that not only the surface sulfur species are thoroughly removed by O₂ but also that most phosphorous atoms in MoP do not run off during the sulfiding treatment. It is most likely that the exchange between S and P does not take place under HDS conditions. Therefore, the structure of MoP may persist while a P- and S-mixed catalytic surface may be formed under HDS conditions. The presence of both P and S atoms could be the main explanation for the unique activity of MoP in hydrotreating reactions, which was also proposed by Webber and co-workers [7].

The activity data (Fig. 5) also show that the MoP/SiO₂ catalyst has stable HDS activity even when treated by H₂S/H₂ at temperatures as high as 623 K. A decline in activity is evident only when the sulfidation temperature is higher than 623 K. IR study (Fig. 9) on the reactivation of the H₂S-sulfided MoP/SiO₂ catalysts is helpful for understanding the sulfiding effect of H₂S/H₂ on MoP/SiO₂. For the catalyst sulfided by H₂S/H₂ at 573 K, the sulfided surface can be converted mostly to phosphide by an H₂ activation at 923 K. This indicates that there exist both reversibly and irreversibly bonded sulfur species on the sulfided catalyst and most sulfur species is reversibly bonded on the surface. The irreversibly adsorbed sulfur species can be removed only by oxidation. This is very similar to the case of thiophene-sulfided MoP/SiO2 catalyst (Fig. 8) where most surface sulfur species can be removed by H₂ reduction at 923 K. For the 773 K-sulfided MoP/SiO2 catalyst (Fig. 9B), the distribution of sulfur species on the surface is different: most sulfur species are irreversibly adsorbed as the band at 2096 cm^{-1} predominates for CO adsorbed on the catalyst reactivated by H₂ at 923 K (Fig. 9B-d). Combining the activity data presented in Fig. 5, one can reasonably deduce that the reversibly bonded sulfur species on MoP/SiO₂ catalysts is not harmful to the catalytic activity while the irreversibly bonded sulfur species could be considered as a poison. Therefore, although both the HDS process and a presulfidation using H₂S/H₂ can lead to the sulfidation of the surface of a MoP/SiO₂ catalyst, the composition of the sulfur species are different. For a MoP/SiO₂ catalyst used in the HDS of thiophene, most sulfur species are reversible adsorbed on the catalyst surface. The detrimental effect of presulfidation (using H₂S/H₂ above 623 K) on the HDS activity of MoP/SiO₂ catalyst (Fig. 5A-f and 5A-g) may arise from the formation of a large portion of irreversibly bonded sulfur species.

IR studies on the reactivation of the sulfided MoP/SiO₂ catalyst also show that a sulfided phosphide catalyst can be completely regenerated by an oxidation and a subsequent reduction. The full regeneration of the phosphide nature of the sulfided catalyst indicates that most P atoms in molybdenum phosphide may not be exchanged or removed by sulfur species under reaction conditions because there is no phosphorous supplied in the reactivation process. This is strikingly different from nitride and carbide catalysts where N and C atoms in molybdenum nitride and carbide were proposed to be displaced by S atoms when they were treated by thiophene/H₂ at HDS temperature [21-23]. For a complete regeneration of sulfided Mo₂N/Al₂O₃ catalysts, NH₃ was needed as a N source to form molybdenum nitride [21]. Thus, it is suggested that the structure of MoP is likely maintained with sulfur species bonded on the top layer under HDS conditions. This again suggests that MoP is a potential substitute for conventional Mo sulfide catalysts in hydrotreating processes.

5. Conclusions

(1) Adsorbed CO on a fresh MoP/SiO₂ catalyst shows a characteristic IR band at 2045 cm⁻¹, which is ascribed to CO linearly bonded to cus Mo^{δ +} (0 < $\delta \leq 2$) sites on the surface of molybdenum phosphide. By analyzing the ν (OH) region in the IR spectra, it is found that P atoms of fresh MoP/SiO₂ are apt to react with oxygen to form phosphate species during the passivation process. The passivation layer on molybdenum phosphide can be removed by H₂ reduction, quite different from the case of molybdenum nitride and carbide catalysts.

(2) HDS activity measurements show that a MoP/SiO_2 catalyst remains stable in the reaction temperature range 593-673 K in the initial reaction stage, though IR spectra of adsorbed CO indicate that the working surface of MoP/SiO₂ catalyst is partially sulfided in HDS reactions. Both reversibly and irreversibly adsorbed sulfur species are present on the MoP/SiO₂ catalyst sulfided by either thiophene/H₂ or H_2S/H_2 . When sulfided in HDS reaction or by H_2S/H_2 at temperatures below 623 K, MoP/SiO₂ still shows stable activity because most surface sulfur species are reversible. The irreversibly bonded sulfur species is deleterious to HDS activity of MoP/SiO₂ catalysts, which could be the reason for the detrimental effect of H₂S presulfidation at temperatures above 623 K. The sulfided MoP/SiO₂ can be fully reactivated to a fresh phosphide catalyst under mild conditions. It is proposed that the structure of MoP may persist while the phosphide surface is modified by sulfur under HDS conditions. Further theoretical calculations on the interaction and reaction between sulfur species and molybdenum phosphide are underway in this laboratory.

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