Dibenzothiophene hydrodesulfurization over MoP/SiO₂ catalyst prepared with sol-gel method

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Abstract−Silica-supported molybdenum phosphide, MoP/SiO₂ catalysts with different Mo weight loadings were prepared by temperature programmed reduction of the oxidic catalyst precursors, which were prepared via sol-gel technique using ethyl silicate-40 as silica source. Samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area measurements, and their catalytic activity in hydrodesulfurization (HDS) was tested with dibenzothiophene (DBT) as model compound. XRD analysis revealed the amorphous nature of the catalyst up to 10 wt% Mo loading and the formation of crystalline MoP phase on amorphous silica support with higher Mo loading. BET surface area showed high surface area for catalysts prepared by sol-gel technique with lower Mo content, and the surface area decreased with increasing in Mo loading. The HDS results showed that prepared MoP/SiO₂ exhibited high HDS activity and stability toward the catalytic test. Among the series of catalysts prepared, MoP/SiO₂ containing 20 wt% Mo was found to be the most active catalyst. And the effects of reaction temperature and hydrogen pressure on conversion and product selectivity were investigated.

Key words: Dibenzothiophene, MoP, Hydrodesulfurization

INTRODUCTION

Catalytic hydrodesulfurization (HDS) is a key process in oil refining schemes for producing clean transportation fuels. Other than traditionally used sulfide catalysts, there is a need to develop better catalysts to meet severe environmental restrictions on the content of sulfur in transportation fuels [1-4]. Transition metal phosphides like MoP [5,6], WP [7], and Ni₂P [8,9] constitute a new class of catalysts that have recently been reported to be active for hydroprocessing reactions. For example, the research of Oyama's [10] laboratory has identified MoP as an active and stable hydroprocessing catalyst. The report by Prins [11] has shown that MoP has six times higher activity in the hydrodenitrogenation (HDN) of ortho-propylaniline than MoS₂/Al₂O₃ catalyst, and studies by Bussell [12] have shown that MoP/SiO₂ has four-times higher activity at 150 h of reaction in the HDS of thiophene than MoS₂/Al₂O₃. These reports exhibited the potential application of transition metal phosphides in hydrotreating processes; on the other hand, these studies indicated that it is important for the usage of support to improve the catalytic activity of catalyst. Up to now, for the preparation of supported MoP catalyst, γ-alumina [13,14], silica [10] or carbon [15], whichever was selected as support, impregnating was selected as the usual technique to prepare supported catalyst. Although the impregnation method is simple, for high loading supported catalyst a repetitious impregnation process is needed, which may lead to the uneven dispersal of the active phase on support.

In the current study, we report the successful synthesis of silica-supported molybdenum phosphide (MoP/SiO₂) via sol-gel method, which has been shown to be a method that increases metal support interactions when the support and active phase are synthesized at the same time, so the repetitious process can be effectively avoided to prepare supported catalyst with high loading. And HDS catalytic activities of these catalysts with dibenzothiophene as model compound are described.

EXPERIMENTAL

1. Sample Preparation

Unsupported molybdenum phosphide was prepared using a procedure reported elsewhere [12,13]. Desired quantities of ammonium paramolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O), and ammonium dihydrogen phosphate (NH₄H₂PO₄) were dissolved in 1 : 1 stoichiometric proportions of metal Mo to phosphorus to form clear solution in distilled water. Then the solution was stirred at room temperature for 12 h, and white solid obtained following drying at 393 K was calcined at 773 K for 5 h in air to give a dark blue solid. Then, the sample was reduced to phosphide catalyst by temperature programmed reduction in hydrogen from room temperature to 623 K at a heating rate of 10 Kmin⁻¹, from 623 K to the final reduction temperature of 873 K at the rate of 1 Kmin⁻¹ and kept at this final temperature for 2 h. After reduction, the sample was cooled to room temperature under a H₂ flow and finally passivated for 12 hours according to the method outlined by reference [16].

MoP/SiO₂ catalysts were prepared with theoretical Mo loadings of 5, 10, 20, and 30 wt%. The solutions of ethyl orthosilicate, distilled water and ethanol with volume ratio 1 : 2 : 2 were stirred at 343 K for 30 min, and then the clear aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O and NH₄H₂PO₄, which were prepared in advance like above mentioned, were added and followed by stirring at 343 K until the gel type compounds were formed. After two days aging for these prepared gels, the silica supported oxide precursors were obtained

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by dried at 393 K and then calcined at 773 K for 5 h in air. The silica-supported MoP catalysts were prepared by temperature programmed reduction of the oxidic catalyst precursors; the progress was similar to that one of preparation of unsupported sample.

SiO₂ sample was synthesized also via sol-gel method. The solution of ethyl orthosilicate, distilled water and ethanol with volume ratio 1 : 2 : 2 was stirred at 343 K for 30 min, then a little ammonia was drop added that followed by stirring at 343 K until hyaloid colloid was formed. After two days aging, the silica support was obtained by drying at 393 K and then calcining at 773 K for 5 h in air.

2. Catalyst Characterization

Crystalline phase of supported samples was determined by X-ray diffraction (XRD) using packed powder method. The XRD patterns were acquired using a XD-3 (Beijing purkinje general instrument Co. Ltd) diffractometer using Ni filtered Cu $K\alpha$ radiation (λ= 1.542 Å) at 36 kV, 20 mA and a scanning range 2θ of 10-80°. Specific surface areas of the samples were evaluated by applying the BET method to the nitrogen adsorption isotherms measured at 77 K. The morphology of the prepared samples was observed by scanning electron microscopy (SEM).

3. Catalytic Activity

The activity measurement for dibenzothiophene HDS was carried out in an electromagnetic stirring autoclave for 1 h. A 1.0 g quantity of the prepared sample without other pretreatment besides powdered in a mortar was added in the autoclave. And the reaction material was 0.5 wt% dibenzothiophene in cyclohexane. The liquid products of HDS were quantitatively analyzed by FID gas chromatogram with a capillary column.

RESULTS AND DISCUSSION

The XRD patterns of all the catalysts prepared by sol-gel with 5, 10, 20 and 30 wt% Mo loadings are shown in Fig. 1. For comparison, the XRD pattern of pure support is also included (Fig. 1(a)). The pattern of silica support gives an amorphous and broad feature
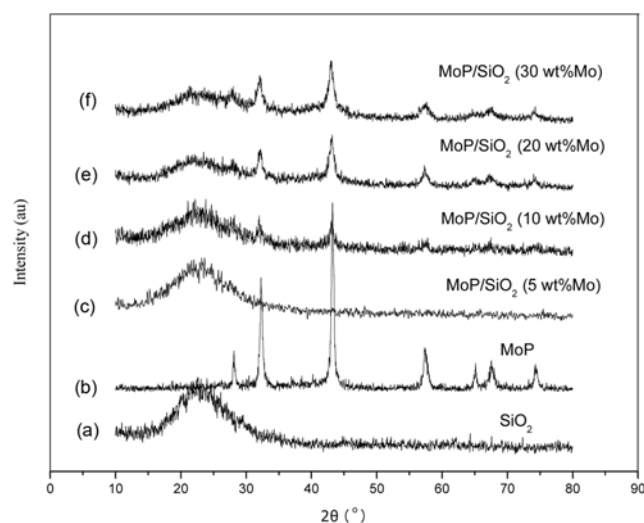

Fig. 1. XRD patterns of (a) SiO₂; (b) passivated MoP (c) passivated MoP/SiO₂ (5 wt% Mo); (d) passivated MoP/SiO₂ (10 wt% Mo); (e) passivated MoP/SiO₂ (20 wt% Mo); and (f) passivated MoP/SiO₂ (30 wt%Mo).

at about 22°, similar to the diffraction pattern of SiO₂ support that was selected to prepare supported catalyst by impregnation method [10,12]. The pattern of unsupported MoP exhibits several peaks at 28.0°, 32.2°, 43.2°, 57.3°, 64.8°, 67.4° and 74.3°, similar to the standard pattern from the JCPDS powder diffraction file (24-0771) as well as that reported in the literature [11,12]. And these peaks are assigned to the {001}, {100}, {101}, {110}, {111}, {102} and {201} reflections of bulk MoP, respectively. For MoP/SiO₂ samples with 20 and 30 wt% Mo loadings, it can be found that the diffraction patterns exhibit similar peaks of bulk MoP, confirming the successful preparation of MoP on the silica support. The MoP/SiO₂ sample (10 wt% Mo) shows weak peaks at 32.2°, 43.2°, 57.3° that are assigned to the features of bulk MoP. The MoP/SiO₂ sample (5 wt% Mo) only shows the features of amorphous silica (Fig. 1(a)). For samples with 10, 20 and 30 wt% Mo loadings, the intensity of diffraction peaks increases with the increasing of Mo loading, and it is interesting to note that even though the MoP is in the crystalline form at higher Mo loading, the silica support still retains its amorphous nature, leading to the high surface area of the catalysts, which indicates that MoP particles are well dispersed on the support when the Mo loading is low; the increase of Mo loading results in the growth or aggregation of MoP crystal particle.

Shown in Fig. 2 is an SEM image of MoP/SiO₂ sample with 30% Mo loading. Inspection of Fig. 2 indicates the presence of MoP particles of a fairly uniform size dispersed on the silica support and
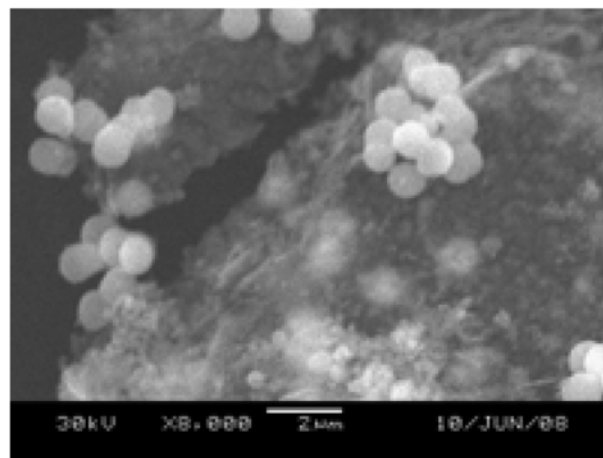

Fig. 2. Scanning electron micrographs (SEM) of MoP/SiO₂ with 30% Mo loading.

Table 1. Surface area of support and MoP/SiO₂ catalysts with different Mo loadings

Mo loading[a] (wt%)	Catalyst phase[b]	S_{BET} (m²g⁻¹)
00	SiO₂	167
10	MoP/SiO₂	139
20	MoP/SiO₂	116
30	MoP/SiO₂	108
Unsupport	MoP	008

[a]Mo loading was determined on the basis of the initial concentration of the ammonium heptamolybdate solution
[b]Catalyst phase determined by XRD patterns

some particles have aggregated together, which is consistent with the XRD analysis result.

The surface areas of support and MoP/SiO₂ samples with different Mo loadings are shown in Table 1. The surface area of bulk MoP is only 8 m^{2}g^{-1}, which was consistent with molybdenum phosphide prepared via temperature programmed reaction as reported by reference [10]. As expected, it is an effective technology to prepare MoP/SiO₂ catalyst with high surface area by sol-gel synthesis using ethyl silicate-40 as the silica source, the surface area can reach 108 m^{2}g^{-1} for 30% Mo loading, and the hope is to further increase the surface area by optimizing the hydrolysis of ethyl silicate-40 [17]. Phillips et al. [12] once reported that the surface area was 89 m^{2}g^{-1} for MoP/SiO₂ catalyst with 15 wt% Mo loading prepared via impregnating method. It can be found that the surface area of catalysts decreases with the increase in Mo loading. It is expected that, as Mo loading is increased, crystalline MoP clusters are formed that cover the amorphous silica support, reducing the total surface area of the catalyst.

Dibenzothiophene (DBT) structures and their alkyl derivatives are the typical sulfur-containing refractory compounds present in feed stocks [18], so DBT was selected as sulfur-containing compound to evaluate the HDS activity of prepared MoP/SiO₂ samples. The main products for HDS of DBT over these catalysts are biphenyl (BP) and cyclohexylbenzene (CHB), and minority tetrahydrodibenzothiophene and bicyclohexyl are also created. So the HDS reaction of DBT on MoP/SiO₂ catalyst may go through two parallel pathways: (1) direct desulfurization to yield BP, and (2) hydrogenation followed by desulfurization to yield CHB, and CHB transformed to bicyclohexyl through deeply hydrogenation. Fig. 3 shows the proposed reaction pathway for HDS of DBT over MoP/SiO₂ catalyst, which is similar to the reports about the HDS pathway of DBT over molybdenum nitride [19], molybdenum carbide [20], et al. It is noteworthy that all MoP based catalysts show a larger HDS activity than the other catalysts, which can be explained in terms of the globular morphology of the MoP active phase [13,21].
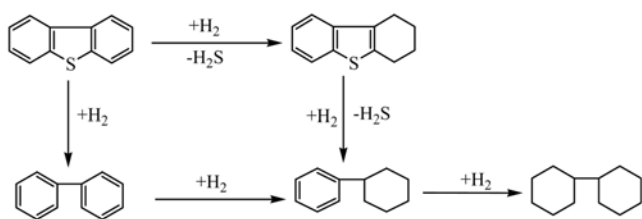
This latter structure offers a larger density of active sites than the layered structure of the traditional MoS₂ phase [21].

Shown in Table 2 are HDS results over MoP/SiO₂ catalysts with different Mo loadings at 573 K and total pressure of 8.0 MPa. For catalysts with 5, 10 and 20 wt% Mo loadings, the HDS activity was found to increase with the increasing in Mo loading, and the catalyst with 20 wt% Mo loading had the highest HDS activity with same HDS condition. However, the catalyst with 30 wt% loading was less active than the 20 wt% loading. Montesinos-Castellanos [21] once reported that for alumina-supported MoP catalysts, the increase in metal loading resulted in the sintering of MoP particles on the support surface and then decreased in specific area, which was found to be detrimental for HDS activity. The selectivity of the desulfurization (BP/CHB ratio) for the sample with 5 wt% Mo loading is low (3.6), but for the other catalysts, it is slightly higher, indicating that all the catalysts with different Mo loadings exhibit a similar selectivity for the desulfurization-hydrogenation. Thus, for HDS of DBT over MoP/SiO₂ catalysts, the main reaction pathway is direct sulfur removal from DBT, while the presence of hydrogenated intermediate indicates that the cyclohexylbenzene is formed via hydrogenation route.

To determine the effect of final reduction temperature on catalytic activity, the HDS results of catalysts prepared with different reduction temperature are shown in Table 3. As seen in Table 3, the sample prepared at lowest temperature (723 K) exhibits the lowest activity, which may be because some MoO₂ was formed at this temperature and oxide precursors were not fully transformed to MoP phase. The largest HDS activity was observed on the catalyst prepared at reduction temperature of 773 K, and the increasing of final reduction temperature resulted in the decrease of activity within the temperature area of 773 to 973 K. The synthesis of MoP catalysts

Table 3. Influence of different final reaction temperature on HDS catalytic activity

Final reaction temperature (K)	Reaction factors		Catalyst phase[a]	Activity (%)
	Temperature (K)	Pressure (MPa)		
723	573	8	MoO₂, MoP/SiO₂	30
773	573	8	MoP/SiO₂	85
873	573	8	MoP/SiO₂	79
973	573	8	MoP/SiO₂	62

[a]Catalyst phase determined by XRD analysis

Fig. 3. Proposed reaction pathways for HDS of dibenzothiophene over MoP/SiO₂ catalyst.

Table 4. Influence of reaction temperature and pressure on the HDS activity of supported catalyst

Catalyst	Reaction factors		Activity (%)	Selectivity (BP/CHB)
	Temperature (K)	Pressure (MPa)		
20 wt%Mo	573	6	58	5.8
20 wt%Mo	573	8	79	4.9
20 wt%Mo	573	11	98	2.8
20 wt%Mo	613	8	91	3.7
20 wt%Mo	633	8	99	3.1

Table 2. Influence of Mo content on the HDS activity of supported catalyst

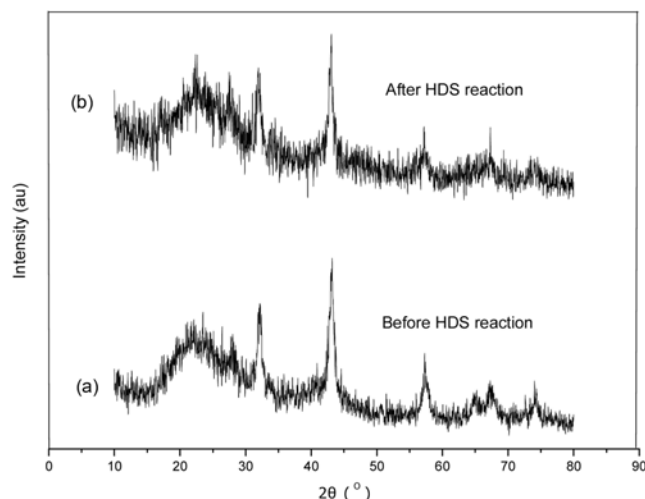| Catalyst	Reaction factors		Activity (%)	Selectivity (BP/CHB)
	Temperature (K)	Pressure (MPa)		
5 wt%Mo	573	8	23	3.6
10 wt%Mo	573	8	56	4.8
20 wt%Mo	573	8	79	4.9
30 wt%Mo	573	8	72	4.1

Fig. 4. XRD patterns of MoO/SiO₂ catalysts with 20 wt% Mo loading before HDS (a) and after HDS (b).

to high reduction temperatures resulted in the sintering of MoP particles with high crystal size, which then may have decreased the HDS activity [13,21]. Considering the selectivity in HDS of DBT reaction, regardless of the final reduction temperature, the similar selectivity was observed for all the MoP/SiO₂ catalysts. This may indicate that the reduction temperature did not affect the selectivity under these reaction conditions.

The influence of hydrogen pressure and reaction temperature on HDS reaction over MoP/SiO₂ (20 wt% Mo loading) was also examined and results are shown in Table 4. The conversion of DBT increases with increasing in hydrogen pressure; however, the BP selectivity decreases with the pressure increasing, which indicates that pressure increasing is favorable for hydrogenation over MoP/SiO₂ catalyst, and some BP can be further hydrogenated to form CHB at high hydrogen pressure which may also decrease the BP selectivity. The increase of DBT conversion and decrease of BP selectivity were also observed with the increasing in reaction temperature.

After HDS reaction, MoP/SiO₂ catalyst with 20 wt% Mo loading was removed from the reactor and analyzed by XRD, and the XRD pattern is presented in Fig. 4. It can be found that after HDS reaction, the XRD pattern is almost the same as that of before HDS, including the peak locations and their relative intensities. There are no other Mo compounds, especially Mo sulfide obvious formation, which indicates the XRD signature of catalyst was not significantly affected by the HDS catalytic reaction. Similar results can be obtained for other MoP/SiO₂ catalysts with 10 and 30 wt% Mo loading (XRD patterns are not supplied), which indicates that these samples prepared by sol-gel technique were stable towards the HDS catalytic test.

CONCLUSIONS

Our results demonstrate that silica-supported molybdenum phos-

phide (MoP/SiO₂) was successfully prepared by temperature programmed reduction of the oxidic catalyst precursors, which was prepared by dried and followed by calcined the gel that formed with ethyl orthosilicate as silicon source. After being reduced, the formation of crystalline MoP phase on amorphous silica support generated an active catalyst for the HDS of DBT, which exhibited high catalytic activity and strong resistance to sulfiding.

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