Synthesis and Performance of Presulfided NiMoP/Al2O3-SiO2 Catalyst

Jingcheng Zhang1, Guoliang Song1, Yuanming Hu3, Haibin Yu1, Guohui Zhang1, Peijiang Zhao2, Jingyuan Huang2, Yanmin Sun1, Tao Yang2, Yuting Zhang1, Jun Nan1, Jinjian Zhu1, Han Xiao1 and Shangqiang Zhang1

1 CNOOC Tianjin Chemical Research and Design Institute, Tianjin, 300131, China; 2 CNOOC Zhoushan Petrochemical Co., Ltd; 3 PetroChina Jilin Petrochemical Company, Jilin, 132000, China; Email: zhangjch7@cnooc.com.cn

Abstract. Presulfided NiMoP/Al2O3-SiO2 catalysts were synthesised. The BET surface area and BJH pore volume gradually decrease with P loading due to the ingress of active phases into the pores of the support. No bulk Ni sulfide phase is observed either in the XRD pattern or in the HRTEM micrographs of all catalysts. The mainly high active center is multilayered Ni-Mo-S type II phase benefited from the weak bond between Al2O3-SiO2 support and active components. The incorporation of phosphorous enhances the dispersion of MoS2 particles and formed more multilayered Ni-Mo-S type II phase. The route of hydrogenation activity increases with the content of P up to 1.2 wt.%, and the route of direct desulfurization activity in the hydrodesulfurization of dibenzothiophene decreases simultaneously. This is attributed to the higher MoS2 stacking number and shorter MoS2 slab length.

1. Introduction
More stringent legislation to limit the sulfur content in transportation fuels has been introduced throughout the world because of the increasing concern about environmental pollution. Generally, hydrotreatment (HDT) reactions are catalyzed by NiMo/Al2O3 catalyst. The active phase of MoS2 nanocrystallites promoted by nickel atoms were well dispersed on a high-surface-specific alumina support. In this sense, different materials have been studied as catalyst supports, specially the mixed oxide supports, such as the Al2O3-TiO2, which facilitate redox processes for the active phases of Mo, and therefore facilitate the formation of active octahedral type sites of the Mo oxide species. Extensive research studies have been dedicated to develop improved catalysts in the mean of the decomposition of ammonium thiomolybdates[1, 2]. It is reported that the activity of the CoMoS/Al2O3 catalysts modifies by introduction of phosphorus, and the behavior of catalyst depends on the phosphorus addition content[3]. In the open literatures, the introduction of phosphorus reduced the strong interaction of Mo metals with Al2O3 support, and prevent the NiAl2O4 species formed. Hence, the catalyst was prepared with a better dispersion of the Mo and promoter atoms, which is attributed to the formation of phosphomolybdate complexes[4].

Effect of phosphorus addition on the behavior of presulfided NiMoP/Al2O3-SiO2 has never been reported. Consequently, This work presents a comparative study of presulfided NiMo/Al2O3 catalysts with different P addition, and thoroughly characterized. The textural, superficial, electronic, and catalytic properties during the HDS of DBT were also investigated.

2. Experimental
2.1. Support and Catalysts Preparation
All reagents of analytical grade in the experiment were purchased from Sinopharm Chemical Reagent Co., Ltd. The presulfided NiMo/Al2O3 catalysts with different P addition was prepared by incipient-wetness co-impregnation of Al2O3-SiO2 ($S_{BET} = 296 \text{ m}^2\text{g}^{-1}$). The Ni and Mo atoms were introduced with the ammonium tetrathiomolybdate and Ni(NO3)2·6H2O, which were separately dissolved in water and then mixed to form a NiMoS solution. The catalyst was dried at 120 °C, and roasted at 350 °C (10 °C/min) for 4-6 h under the flow of nitrogen gas. The presulfided NiMoP/Al2O3-SiO2 catalysts contain 20 wt.% MoO3, 4 wt.% NiO and a various P content. These catalysts are labeled as NiMoP-X, X denoting the P content.

2.2. Catalysts Characterization
The textural properties for the presulfided NiMoP/Al2O3-SiO2 catalysts were determined from the adsorption-desorption isotherms of nitrogen, which performed with a Micromeritics TriStar 3000 system at -196 °C. Previous to their measurements, the samples were treated at 200 °C for 2 h under vacuum. The specific surface areas were calculated by means of BET model, and the pore volume were calculated by means of BJH model.

The XRD determinations for the presulfided NiMoP/Al2O3-SiO2 catalysts were recorded in a Panalytical X’ Pert Pro MPD diffractometer, the configuration is as follows: a curved graphite monochromator, equipped with Cu-Kα radiation ($\lambda = 1.5406 \text{ Å}$) operating at 45 kV and 40 mA at a scanning rate of 5 min$^{-1}$. The HRTEM measurement of materials was carried out in a JEM-2100 analytical microscope, which operated at 200 kV.

2.3. Catalytic Activity Measurement
In this work, the catalytic activity measurement was carried out in a high-pressure reactor, using DBT as model compound, the reaction condition is as follows: 260 or 280 °C, 2.0 MPa, liquid hourly space velocity 2 h$^{-1}$, and the H2/feed ratio is 300/1. The reaction product mixture was analyzed by an Agilent HP 7890 GC equipped with a flame ionization detector and CP-5 capillary column. The reaction time averaged was 12 hours and the reaction product samples were taken every 2 h and analyzed by chromatography on a Agilent HP 7890 GC instrument equipped with a FID detector and CP-5 capillary column (30 m × 0.32 mm i.d.).

The HDS of DBT yields two main products: biphenyl (BP) and cyclohexylbenzene (CHB), which through the so-called direct desulfurization pathway (DDS) and the hydrogenative pathway (HYD), respectively. The total, DDS and HYD activities were calculated according to the following equations:

\[ A_{\text{Total}} = \frac{F_0 X}{m} \]  \hspace{1cm} (1)
\[ A_{\text{DDS}} = A_{\text{Total}} S_{\text{BP}} \]  \hspace{1cm} (2)
\[ A_{\text{HYD}} = A_{\text{Total}} S_{\text{CHB}} \]  \hspace{1cm} (3)

Where $A_{\text{Total}}, A_{\text{DDS}}, A_{\text{HYD}}$ are the total, DDS and HYD activity, respectively. $F_0 = \text{flow rate of DBT (mol/s)}, X = \text{conversion of DBT}, m = \text{mass of catalyst (Kg)}, S_{\text{BP}} = \text{selectivity of BP}, S_{\text{CHB}} = \text{selectivity of CHB}.$

3. Results and Discussion

3.1. Catalysts characterization
Fig. 1 shows the XRD patterns of presulfided NiMoP/Al2O3-SiO2 catalysts. the weak reflections at 14.4°, 33°, 40° and 58° are observed, which are assigned to the characteristic reflections (002), (101), (103) and (110) of 2H-MoS2 structure. The crystalline is poor, which indicate a better dispersion of the MoS2 species. The characteristic reflections of nickel sulfide phases are not shown in all the XRD patterns of the catalysts, which indicated that Ni atoms are highly dispersed on the edge or corner sites.
of the MoS$_2$ structure. The effect of P on the nickel sulfide is not found and not agreed with the research conclusions of Nava, who reported that the P species promoted the crystallization of nickel sulfide in unsupported Ni–Mo–W sulfide catalysts with high Ni/Mo atom rate[5].

![XRD patterns](image1)

**Fig. 1.** XRD patterns of presulfided NiMoP/Al$_2$O$_3$-SiO$_2$ catalysts  
\(a, \text{NiMoP-0}/\text{Al}_2\text{O}_3\)-SiO$_2\)  \(b, \text{NiMoP-0.6}/\text{Al}_2\text{O}_3\)-SiO$_2\)  \(c, \text{NiMoP-1.2}/\text{Al}_2\text{O}_3\)-SiO$_2\)  \(d, \text{NiMoP-1.8}/\text{Al}_2\text{O}_3\)-SiO$_2$

Fig. 2 shows the FT-IR spectra of presulfided NiMoP/Al$_2$O$_3$-SiO$_2$ catalysts adsorbed pyridine. The 1541 cm$^{-1}$ peaks and 1449 cm$^{-1}$ peaks are assigned to Brønsted acid sites and Lewis acid sites, respectively. It is obvious by comparison the peak intensities that the amount of both the Brønsted and Lewis acid sites increase with the P addition in our study. Brønsted acid sites contain that from the Al$_2$O$_3$ surface and that generated at sulfided catalyst by dissociation of H$_2$S on anion vacancies of MoS$_2$. In this study, the effect of P on the acidity of support may be very little because P is added after the impregnation of Mo. So it can be deduced that phosphorous favors the formation of in-situ generated Brønsted acid sites. Also the increase intensities of the peak at 1449 cm$^{-1}$ suggests that more anion vacancies of MoS$_2$ are formed on the presulfided NiMoP/Al$_2$O$_3$-SiO$_2$ catalyst.

![Py-IR spectra](image2)

**Fig. 2.** Py-IR spectra of presulfided NiMoP/Al$_2$O$_3$-SiO$_2$ catalysts  
\(a, \text{NiMoP-0}/\text{Al}_2\text{O}_3\)-SiO$_2\)  \(b, \text{NiMoP-0.6}/\text{Al}_2\text{O}_3\)-SiO$_2\)  \(c, \text{NiMoP-1.2}/\text{Al}_2\text{O}_3\)-SiO$_2\)  \(d, \text{NiMoP-1.8}/\text{Al}_2\text{O}_3\)-SiO$_2$

The textural properties of the presulfided NiMoP/Al$_2$O$_3$-SiO$_2$ catalysts are given in Table 1. It is observed that the SSA progressively decrease with the increase of P concentration. However, the
further increase of P concentration from 1.2 wt.% to 1.8 wt.% causes a evident decrease in SSA, the pore capacity and pore diameter. The possible explanation is that the pores of the Al₂O₃-SiO₂ supports are blocked partially by the MoS₂ crystal particles. By comparing the pore size distributions curves of series catalysts samples, it is also indicated mainly that the (002) planes of the MoS₂ crystallites are basal-bonded on the (111) Al₂O₃-SiO₂ surface. A characterization of dual porosity distributions curves and the down trend of pore volume with increasing of P concentration, indicating that phosphorus species deposited in the pore of catalysts with high P concentration.

Table 1 textural properties of presulfided NiMoP/Al₂O₃-SiO₂ catalysts

| Samples                  | BET (m²·g⁻¹) | Pore volume (cm³·g⁻¹) | Pore diameter (nm) |
|--------------------------|--------------|-----------------------|--------------------|
| NiMoP-0/Al₂O₃-SiO₂       | 172          | 0.38                  | 7.4                |
| NiMoP-0.6/Al₂O₃-SiO₂     | 166          | 0.35                  | 7.0                |
| NiMoP-1.2/Al₂O₃-SiO₂     | 152          | 0.30                  | 6.6                |
| NiMoP-1.8/Al₂O₃-SiO₂     | 138          | 0.28                  | 6.4                |
| Al₂O₃-SiO₂ Support      | 296          | 0.71                  | 8.9                |

Figure 3 shows representative HRTEM micrographs of the presulfided NiMoP/Al₂O₃-SiO₂ catalysts, the P concentration is 0 and 1.2, respectively. The black short stripes are observed in the two micrographs and assigned to the MoS₂ or Ni-Mo-S slabs. These slabs are homogeneously dispersed on the catalyst surfaces. There is no exceptionally large aggregates, suggesting good dispersion of MoS₂ or Ni-Mo-S crystallites. Comparing the two catalysts, the NiMoP-1.2/Al₂O₃-SiO₂ shows better layer numbers and slab length. Two or three layers are detected in most of the MoS₂ slabs of the sample.

Fig. 3. HRTEM micrographs of presulfided NiMoP/Al₂O₃-SiO₂ catalysts, (a) NiMoP-0/Al₂O₃-SiO₂ and (b) NiMoP-1.2/Al₂O₃-SiO₂

A quantitative comparison was made by statistical analysing the slab length and slab number of black short stripes, including more than 300 slabs taking from different parts of micrographs of the same catalyst. Statistical data is listed in Table 2. It is clear that the addition of P into presulfided NiMoP/Al₂O₃-SiO₂ catalyst plays a positive role in dispersing well of MoS₂ or Ni-Mo-S crystallites. The presulfided NiMoP/Al₂O₃-SiO₂ catalyst shows a smaller slab than that without P addition. With the increase of P content from 0 to 1.2 wt.%, the average slab number increases from 2.4 to 2.7, and meanwhile the slab length decreases from 2.4 to 2.3 nm. With further increase of P content, the average slab number shows no more change, while the average slab length increases notably to 2.5 nm, probably due to large aggregates of MoS₂ crystallites.

Table 2 Statistical analyse data of MoS₂ crystallite stack of various catalyst samples

| Samples                  | N  | L (nm) |
|--------------------------|----|--------|
| NiMoP-0/Al₂O₃-SiO₂       | 2.4| 2.4    |
| NiMoP-0.6/Al₂O₃-SiO₂     | 2.5| 2.4    |
It is reported that NiMo/Al₂O₃ catalyst prepared with oxide precursor generally shows single-slab and few three-dimensional multilayered slabs structures[6]. Whereas the stacking number in presulfided NiMoP/Al₂O₃-SiO₂ catalyst with ATTM precursor is much higher. It is due to the lower interaction metal with support, which leads to the formation of smaller particles of MoS₂. In a word, the promotional effect of P on presulfided NiMoP/Al₂O₃-SiO₂ catalyst is clear. With the proper P content is added, the dispersion of MoS₂ is enhanced, the slab number is higher and the slab length is shorter, which means more type II MoS₂ phase.

### 3.2. Activity evaluation

![Figure 4. HDS activity of DBT on presulfided NiMoP/Al₂O₃-SiO₂ catalysts](image)

The HDS results of DBT on P incorporated presulfided NiMoP/Al₂O₃-SiO₂ shows in Fig. 4. The react temperature is at 260 ℃ in the work. The total activity of DBT maintains the similar level. However, the HYD activity and DDS activity change obviously with the P content. It is clear that \( A_{HYD} \) increases while \( A_{DDS} \) decreases. The P content of 1.2 wt.% is an important inflection point. With the further increase of P content, \( A_{HYD} \) and \( A_{DDS} \) change slightly. It may be the enhanced MoS₂ dispersion, not the enhanced acidity over P-promoted NiMo/Al₂O₃ catalyst affects the product distribution because there is no cracking or methyl-migration reaction in the HDS of DBT. The possible explanation is that DDS and HYD in HDS reaction take place on different active sites on the MoS₂ crystallites of sulfided CoMo or NiMo/Al₂O₃[7]. The DDS route involves non-coplanar adsorption of the sulfur atom at the σ-sites, while HYD of the aromatic ring proceeds via flat adsorption through the π-electrons of the aromatic rings at the τ-sites. Kasztelan[8] has reported that HYD occurs on the corner sites with higher unsaturation and DDS on the edge sites with lower unsaturation on promoted Mo/Al₂O₃ catalyst. Our result can be interpreted with the rim-edge model. When P is incorporated, the corners and rims that allow HYD to occur increase because the dispersion of MoS₂ slabs is enhanced. Comparing the activity of DBT on NiMoP-1.2 and NiMoP-1.8 catalysts, it can be deduced that it is the longer slab length results in a poorer MoS₂ dispersion accounts for the reduced HYD activity at larger phosphorus content.

### 4. Conclusion

Phosphorous influences the catalyst properties mainly in the morphology of Ni-Mo-S phase and the acidity. With the proper P content (1.2 wt.%), the stacking degree increases and the slab length

| Catalyst          | Slab Number | Slab Length |
|-------------------|-------------|-------------|
| NiMoP-1.2/Al₂O₃-SiO₂ | 2.6         | 2.3         |
| NiMoP-1.8/Al₂O₃-SiO₂ | 2.6         | 2.5         |

Note: N, average slab number; L, average slab length

The HDS results of DBT on P incorporated presulfided NiMoP/Al₂O₃-SiO₂ shows in Fig. 4. The react temperature is at 260 ℃ in the work. The total activity of DBT maintains the similar level. However, the HYD activity and DDS activity change obviously with the P content. It is clear that \( A_{HYD} \) increases while \( A_{DDS} \) decreases. The P content of 1.2 wt.% is an important inflection point. With the further increase of P content, \( A_{HYD} \) and \( A_{DDS} \) change slightly. It may be the enhanced MoS₂ dispersion, not the enhanced acidity over P-promoted NiMo/Al₂O₃ catalyst affects the product distribution because there is no cracking or methyl-migration reaction in the HDS of DBT. The possible explanation is that DDS and HYD in HDS reaction take place on different active sites on the MoS₂ crystallites of sulfided CoMo or NiMo/Al₂O₃[7]. The DDS route involves non-coplanar adsorption of the sulfur atom at the σ-sites, while HYD of the aromatic ring proceeds via flat adsorption through the π-electrons of the aromatic rings at the τ-sites. Kasztelan[8] has reported that HYD occurs on the corner sites with higher unsaturation and DDS on the edge sites with lower unsaturation on promoted Mo/Al₂O₃ catalyst. Our result can be interpreted with the rim-edge model. When P is incorporated, the corners and rims that allow HYD to occur increase because the dispersion of MoS₂ slabs is enhanced. Comparing the activity of DBT on NiMoP-1.2 and NiMoP-1.8 catalysts, it can be deduced that it is the longer slab length results in a poorer MoS₂ dispersion accounts for the reduced HYD activity at larger phosphorus content.

### 4. Conclusion

Phosphorous influences the catalyst properties mainly in the morphology of Ni-Mo-S phase and the acidity. With the proper P content (1.2 wt.%), the stacking degree increases and the slab length
decreases comparing with P free catalyst. With a further addition of P content, the dispersion of MoS$_2$ slabs decreases as the slab length increases notably. The performance of the HDS of DBT on different catalysts reveals that the MoS$_2$ particles with higher stacking and shorter slab length have better HYD activity.

References
[1] J.R. Grzechowiak, J. Rynkowski, I. Wereszczako-Zielińska, Catal. Today, 65 (2001) 225-231.
[2] S. J. Tauster, T. A. Pecoraro and R. R.Chianelli, J. Catal. 63, 515 (1980).
[3] S. W.Weller, P.T.Vasudevan, J. Catal. 99, 235 (1986).
[4] P. Atanasova, T. Tabakova, Ch. Vladov, T. Halachev and A. L. Agudo, Appl. Catal. A 161, 105 (1997).
[5] H. Nava, J. Espino, G. Berhault and G. Alonso-Nuñez, Appl. Catal. A 302, 177 (2006).
[6] D. Ferdous, A. K. Dalai, J. Adjaye and L. Kotlyar, Appl. Catal. A 294, 80 (2005).
[7] M. Houalla, D.H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. de Beer, B.C. Gates, H. Kwart, J. Catal. 61 (1980) 523-527.
[8] S. Kasztelan, H. Toulhoat, J. Grimblot and J. P. Bonnelle, Appl. Catal. A 13,127 (1984).