



# Study on the sulfurization of molybdate catalysts for slurry-bed hydroprocessing of residuum

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## Abstract

Sulfurization remarkably affects the physical and chemical properties of dispersed catalysts. In this study, molybdate is taken as catalyst precursor for slurry-bed hydroprocessing of residuum to study the mechanics of sulfurization. Several conditions are used to evaluate the activities of the sulfurized catalysts, and XRD, TEM and BET are employed to characterize the sulfurized catalysts. The results show that molybdate is firstly transferred into some kind of crystallized oxothiomolybdate and then mainly into micro-crystallized MoS<sub>2</sub> in the end. The dispersivity of the MoS<sub>2</sub> granules is greatly enhanced compared to the oxothiomolybdate. XPS analysis shows the portion of Mo<sup>IV</sup> in molybdenum species on the surface of the catalysts is enhanced by the addition of NH<sub>4</sub>Cl during sulfurization. Therefore, the catalytic activity, measured using anthracene as chemical probe in the practical reaction system of hydroprocessing for residue, is also enhanced.

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## 1. Introduction

The slurry-bed hydroprocessing for residue is a newly developed technique for the processing of heavy oils [1]. In this technique, catalysts are dispersed into tiny-sized granules which suspend in the feedstock oil [2–4] instead of being packed in the bed layer of the reactor, thus the problem of deactivation of the catalyst caused by coke formation or poisoning can be ignored. On the other hand, since the catalysts are used for once only, its cost has become the major factor that decides its prospect in the industrial application.

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Most of the slurry-bed hydroprocessing catalysts need to be pre-sulfurized to sulfides with high catalytic activity [5–8], such as pyrrhotine for ferrous salt [8], MoS<sub>2</sub> for molybdate [5–7], etc. Thus it becomes a major study direction to speed the sulfurization, to promote the sulfurization ratio and to improve the dispersivity of the sulfurization products.

Many catalyst precursors for slurry-bed hydroprocessing are water-soluble, such as ferrous salts, nickel salts or molybdates, which are readily resolved in water and react with water-soluble sulfides in solution, thus it may be a good idea to perform the sulfurization based on these reactions. But the mechanics and the methods for the sulfurization is still not very clear. Thus a study about this problem is carried out.

## 2. Experimental

### 2.1. Raw material and used catalysts

Kelamayi Vacuum Residue (KVR) is taken as source oil for hydroprocessing. The typical characteristics of KAR are shown in Table 1. Ammonium heptmolybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] is taken as test sample of catalyst precursor. Sodium sulfide [Na<sub>2</sub>S·9H<sub>2</sub>O] and ammonium chloride [NH<sub>4</sub>Cl] are taken as sulfurizer and auxiliary reagent for sulfurization, respectively. Span-80 is taken as emulsion reagent, and anthracene is taken as chemical probe.

ZN-600 lubricant base oil and Kelamayi Atmospheric Residue (KAR) is taken as dispersion media for simulating KVR. The typical characteristics of KAR are shown in Table 1.

### 2.2. Steps of the experiment

The feedstock oil or dispersion media is mixed with emulsifier in the NGJ-2 slurry-stirrer (heated if necessary) and then the solution of catalyst precursor is added

Table 1  
General properties of KAR and KVR

Residue	$\rho$ (20 °C), g cm <sup>-3</sup>	$\nu$ (100 °C), mm <sup>2</sup> s <sup>-1</sup>	$w$ (carbon residue), %	Molecular weight (VPO)	$N_H/N_C$
KAR	0.9442	108.7	2.0	470	1.73
KVR	0.9609	1110	11.0	950	1.62

Residue	$v$ , %				$w$ (SARA), %			
	C	H	N	S	Saturates	Aromatics	Resin	<i>n</i> -C <sub>7</sub> Asphaltene
KAR	86.6	12.5	0.41	0.13	50.4	22.2	27.2	0.2
KVR	87.1	11.9	0.63	0.24	35.3	25.6	38.3	0.8

dropwise, after being stirred, the solution of sulfurizer (or the mixture of sulfurizer and auxiliary reagent, if needed) is added using the same method. After stirring for a specific time, the mixture is heated to 140 °C and bubbled with nitrogen to remove the water.

In order to evaluate the hydrocracking activity of the catalysts, hydroprocessing is carried out using a 20/450TFYX-01 autoclave. A specific amount of source oil or dispersion material with sulfurized catalysts dispersed in is fed to the autoclave, which is then charged with hydrogen to 7.0 MPa under normal temperature and heated to 420 °C. After 60 min, the reactor is cooled with water to cease the hydroreaction. The products are leached, and the solids are extracted with hot toluene to obtain the toluene-insoluble, i.e. the coke, which is dried and weighed; the filtrate liquor is distilled to get the naphtha fraction (<150 °C), light gas oil (150–350 °C), vacuum gas oil (350–450 °C) and distilled bottom (>450 °C) [2].

Chemical-probe method is a good way to measure the ability of activating hydrogen of the catalysts [4]. Anthracene is taken as chemical probe. The feedstock oil with sulfurized catalyst dispersed in is mixed with anthracene with a weight ratio of oil/anthracene 20:1, and the mixture is heated in the presence of hydrogen whose initial pressure is 7.0 MPa in the autoclave under 420 °C for 60 min. The products obtained are then leached and the filtrate liquor is distilled to get the fraction with a boiling range of 200–350 °C, which is dissolved in toluene and then examined with gas chromatogram to measure the ratio of the anthracene converted into 9,10-dihydroanthracene.

The quantities of the additions are defined as follows:

- (1) The amount of precursor is marked by the weight ratio of metal that it contains to the feedstock oil;
- (2) The amount of sulfurizer is marked by the molar ratio of the sulfur it contains to the metal that the precursor contains;
- (3) The amount of auxiliary sulfurization reagent (NH<sub>4</sub>Cl) is marked by the molar ratio of auxiliary sulfurization reagent to Mo element in molybdate.

The TYX series of autoclaves are used as reactor for thermal treatment under hydrogen or hydrocracking. Sulfurization products are centrifuged from source oil or dispersion media with a rotation speed of 4500 rpm for 30 min, and then washed with toluene and oxygen-free deionized water in turn.

### 2.3. Characterization of sulfurized catalysts

The following methods are employed to characterize the sulfurization catalysts:

- (1) XRD, using a D/MAX-III A diffractometer;
- (2) XPS, using a Microlab MKII Photoelectron Spectrometer. To determine the composition quantitatively. MoS<sub>2</sub> (Chemical Pure) yielded in Beijing Shuang-huan Chemical Reagent factory) is used as external reference;
- (3) TEM, using a DEL-1200EX Transmission Electron Microscopy;
- (4) BET, using an ASAP-1200 Absorption–desorption meter.

#### 2.4. Outline of mechanics study

The sulfurization of catalyst precursor has to go through two stages, i.e. dispersion and heating in the presence of hydrogen. To clarify the changes that take place respectively in these two stages, the sulfurization is carried out in three stages, i.e.

Stage 1. Precursors are sulfurized directly in water-solution;

Stage 2. Precursors are sulfurized in water–oil emulsification;

Stage 3. The sulfurized catalysts dispersed in the media is heated in the presence of hydrogen.

### 3. Results and discussion

#### 3.1. XRD analysis

In the sulfurization of molybdate solution, the water-insoluble sulfurization products are hardly obtained in stage 1. In stage 2, some yellowish powder, 97% of which is water-soluble, is obtained, whose XRD pattern (Fig. 1) shows some unidentified diffraction peaks according to the Powder Diffraction File (PDF). It is deduced from Fig. 1 that the sulfurized product of molybdate solution is probably oxothiomolybdate. After being heated under hydrogen (stage 3), the patterns of catalysts (Fig. 2) show the diffraction peaks at  $2\theta = 14^\circ(003)$ ,  $33^\circ(101)$ ,  $59^\circ(110)$ . When the auxiliary reagent ( $\text{NH}_4\text{Cl}$ ) added in the sulfurization increases from four times the amount of reactant to eight times amount of reactant, the strength of the  $\text{MoS}_2$  peaks become weaker while the half maximum height width (HMHWH) become wider, which shows that the degree of crystallization is lower and the size of the crystallite becomes smaller. When KAR is taken as dispersion media, almost all the sub-strong diffraction peaks disappear, only leaving the strongest (003), with a very wide HMHW showing its very small crystallite sizes. The result can be explained by viscosity of media, because higher viscosity reduces the crystal degree of  $\text{MoS}_2$ . In whole, the heating prominently changes the composition and the crystallization status of the sulfurization product of the molybdate, and accordingly reduces its crystallization degree.

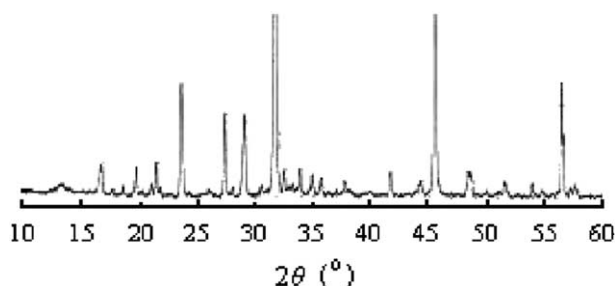


Fig. 1. XRD pattern of the sulfurization product of molybdate before heating under hydrogen.

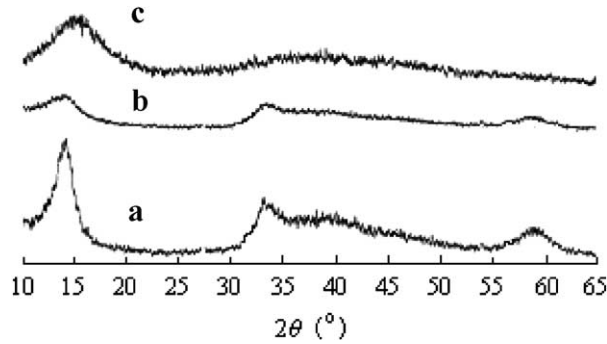
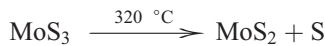
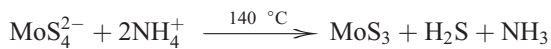
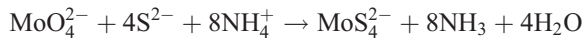
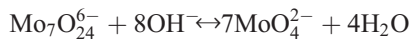


Fig. 2. The XRD patterns of the sulfurization product of the molybdate after the heating under hydrogen. (a)  $\text{NH}_4\text{Cl}$  is added in the four times molar amount of Mo, lubricant is used as dispersion media. (b)  $\text{NH}_4\text{Cl}$  is added in the eight times molar amount of Mo, lubricant is used as dispersion media. (c)  $\text{NH}_4\text{Cl}$  is added in the eight times molar amount of Mo, KAR is used as dispersion media.

The reactions of sulfurization of molybdate in the water soluble can be carried out according to the route shown below [9–11]:



The crystallite size can be calculated according to Scherrer's equation:  $D = 0.89\lambda / B \cos\theta$ . So it is deduced that the crystallite size of oxothiomolybdate yielded through the sulfurization of molybdate is more than 20 nm, while that of  $\text{MoS}_2$  is only 2.0–6.6 nm (as shown in Table 2), which are gotten in Figs. 1 and 2, respectively, according to Scherrer's equation. When ammonium chloride is added to aid the sulfurization, the crystallite size decreases, and it continues to fall when KAR is taken as dispersion media instead of lubricant. So viscosity of the dispersion media is an important factor which effects crystallization of the  $\text{MoS}_2$ .

Table 2  
Crystallite sizes of sulfurization products of molybdate

Amount of $\text{NH}_4\text{Cl}$ used (times molar amount of Mo)	Dispersion media	Crystallite size, nm
4	Lubricant	6.6
8	Lubricant	3.6
8	KAR	2.0

### 3.2. XPS analysis

XPS analysis of the sulfurization products of molybdate is carried out. The Mo species on the surface of the products exhibits two main peaks at Binding Energy (B.E.) 229.0 and 232.5 eV, respectively. The pure MoS<sub>2</sub> (C.P.) exhibits peaks at 229.0 eV (3d<sub>5/2</sub>) and 232.4 eV (3d<sub>3/2</sub>), with an area ratio of 1:0.81, while MoO<sub>3</sub> exhibit 232.6 eV (3d<sub>5/2</sub>) and 235.8 eV (3d<sub>3/2</sub>), with an area ratio of 1:0.68. It is thus assumed that the peak at 229.0 eV represents the presence of Mo<sup>IV</sup>, while that at 232.5 eV is the result of the empiétement of the 3d<sub>3/2</sub> peak of Mo<sup>IV</sup> and 3d<sub>5/2</sub> peak of Mo<sup>VI</sup>. To examine this hypothesis, the area ratio of the peak at 229.0 eV to the peak at 232.5 eV in the XPS pattern of the sulfurization products is also measured to be 1:0.96 in the case of eight times of NH<sub>4</sub>Cl is used and 1:1.20 in the case of four times of NH<sub>4</sub>Cl is used. These are all above that of the pure MoS<sub>2</sub>, which agrees well with the hypothesis described above. Thus it can be deduced that the ratio of the Mo<sup>VI</sup> to Mo<sup>IV</sup> is 0.15:1 and 0.39:1, respectively. According to the quantification model of XPS by Ghosh [12]:

$$I = KN = K_0 E_K^n \sigma N$$

The intensity ( $I$ ) of the certain peak is related to the kinetic energy ( $E_K$ ) of the photoelectron, the photoelectron cross section ( $\sigma$ ) and the concentration of the relative element ( $N$ ), and  $K_0$  is a constant related to the equipment employed.  $E_K$  can be calculated from Einstein's equation about photoemission, and  $\sigma$  is same for the case of Mo<sup>IV</sup> 3d<sub>5/2</sub>

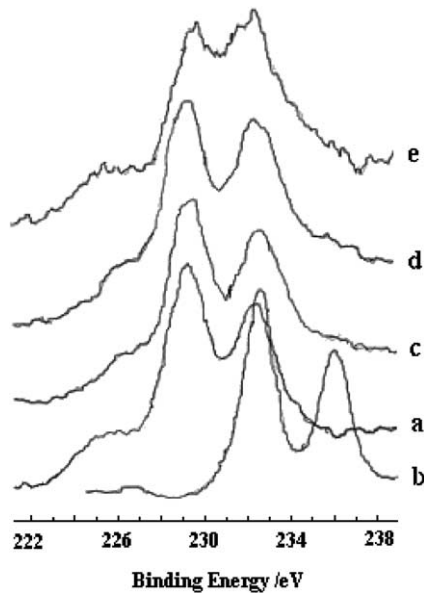


Fig. 3. XPS patterns of the sulfurization products of molybdate, Mo 3d region. (a) MoS<sub>2</sub> (C.P.). (b) MoO<sub>3</sub>. (c) NH<sub>4</sub>Cl is added in the four times molar amount of Mo, lubricant is used as dispersion media. (d) NH<sub>4</sub>Cl is added in the eight times molar amount of Mo, lubricant is used as dispersion media. (e) NH<sub>4</sub>Cl is added in the eight times molar amount of Mo, KAR is used as dispersion media.

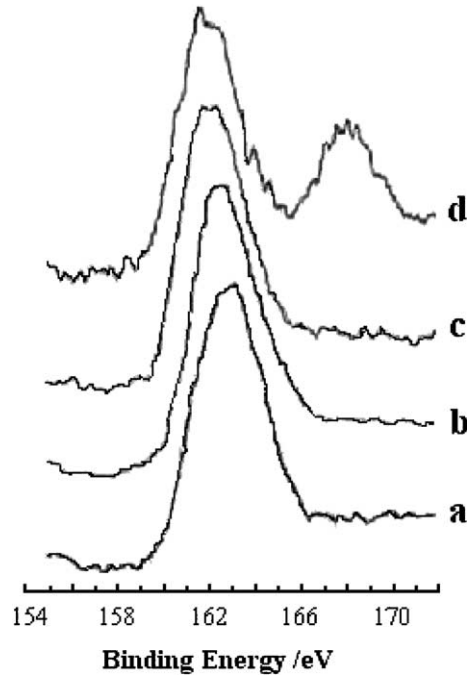


Fig. 4. XPS patterns of the sulfurization products of molybdates, S 2p region. (a) MoS<sub>2</sub> (C.P.). (b) NH<sub>4</sub>Cl is added in the four times molar amount of Mo, lubricant is used as dispersion media. (c) NH<sub>4</sub>Cl is added in the eight times molar amount of Mo, lubricant is used as dispersion media. (d) NH<sub>4</sub>Cl is added in the eight times molar amount of Mo, KAR is used as dispersion media.

peak and the same peak of Mo<sup>VI</sup>, thus the ratio of the concentration of Mo<sup>IV</sup> in the total molybdenum compounds can be calculated to be 71.6% and 86.5%.

As to the ratio of the quantity of S element to Mo element, the intensity ratio of the S and Mo,  $I_S/I_{Mo}$ , is measured. Here  $I_S$  refers to the total area of the S<sub>2p</sub> band, while  $I_{Mo}$  refers to the sum of areas of 229.0 and 232.5 eV peaks, then subtracted by the area of Mo<sup>IV</sup> 3d<sub>5/2</sub> peak, which is calculated as described above, and  $I_S/I_{Mo}$  is relative to the concentration ratio as the following:

$$c_S = N_S/N_{Mo} = I_S K_S / I_{Mo} K_{Mo} = (I_S / I_{Mo}) / (K_S / K_{Mo})$$

With the help of software Origin 6.0,  $I_S/I_{Mo}$  have been obtained from Figs. 3 and 4. The results are 1.410 for MoS<sub>2</sub>, 1.387 for the product obtained when eight times of NH<sub>4</sub>Cl is

Table 3  
The properties of the surficial composition of the sulfurization products of molybdate

Amount of NH <sub>4</sub> Cl used (times molar amount of Mo)	Proportion of Mo <sup>IV</sup> ( $c_{Mo^{IV}}$ ), %	S/Mo ratio ( $N_S/N_{Mo}$ )	Sulfurization ratio ( $c'_S$ ), %
4	71.6	1.960	85.8
8	86.5	1.967	92.3

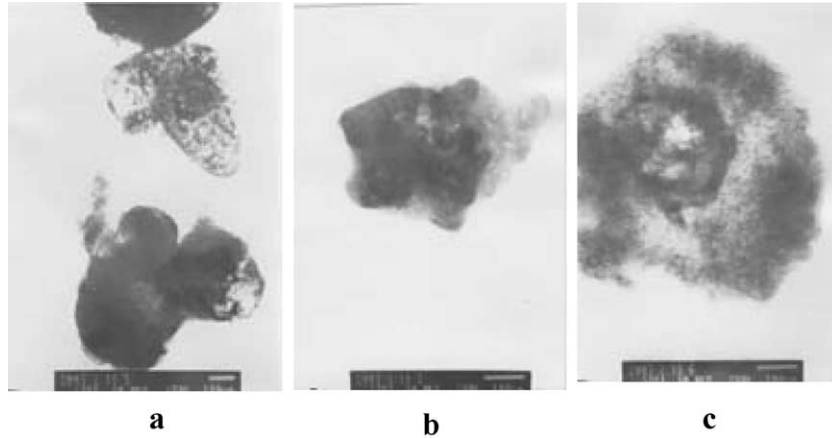


Fig. 5. TEM patterns of granules of sulfurization products of molybdate. (a) Without heating under hydrogen, lubricant used as dispersion media,  $50\,000\times$ . (b) heated under hydrogen, lubricant used as dispersion media,  $80\,000\times$ . (c) Heated under hydrogen, KAR used as dispersion media,  $80\,000\times$ .

used and 1.382 for the case of four times of  $\text{NH}_4\text{Cl}$  is used. Thus it is calculated that  $N_S/N_{\text{Mo}}$  is 1.967 and 1.960 in these two cases, respectively. It is shown that the  $N_S/N_{\text{Mo}}$  ratio is not in the direct proportion with the proportion of  $\text{Mo}^{\text{IV}}$ , thus it is deduced that the Mo species containing sulfur does not exist only as  $\text{MoS}_2$ . Thus the surficial sulfurization ratio is defined as the ratio of the actual sulfur concentration to the concentration of sulfur that molybdenum can maximally combine. This sulfurization ratio can be calculated as follows:

$$c'_s = \frac{N_S}{N_{\text{Mo}}[2c_{\text{Mo}^{\text{IV}}} + 3(1 - c_{\text{Mo}^{\text{IV}}})]}$$

Thus some properties related to the surficial composition of the sulfurization products of molybdate is shown in Table 3.

It is shown that the when the amount of  $\text{NH}_4\text{Cl}$  is doubled, the S/Mo ratio does not change very much while the proportion of  $\text{Mo}^{\text{IV}}$  is increased, and thus the total sulfurization ratio also rises.

### 3.3. TEM analysis

The TEM observations of the sulfurization products of molybdate are shown in Fig. 5. Before heating under hydrogen, the sulfurized catalyst exhibit a morphology of compact

Table 4  
Specific surface area of the sulfurization products of molybdate after heating under hydrogen

Amount of $\text{NH}_4\text{Cl}$ used (times molar amount of Mo)	Dispersion media	Specific surface area, $\text{m}^2\cdot\text{g}^{-1}$
4	lubricant	55.6
8	lubricant	61.7
8	KAR	92.4



Table 5  
The change in hydrogen-transfer ability of the sulfurization products with the amount of  $\text{NH}_4\text{Cl}$  varies

$\text{NH}_4\text{Cl}$ added (times molar amount of Mo)	Conversion of ANT, %
0	34.1
4	38.8
6	41.7
8	42.2

granules which adhere to each other, with the particle size of about 200 nm, and turn into relative loose granules with the particle size of 50 nm after the heating. It is also shown that when the dispersion media is changed from lubricant to KAR, the granules become even looser, and exhibit cotton-like block without core, with the particle size of about 300 nm.

### 3.4. BET analysis

The specific surface area of the sulfurization products are measured using BET method. The result is shown in Table 4. It is shown that when using lubricant as dispersion media, the specific surface area increases along with the quantity of  $\text{NH}_4\text{Cl}$  used; and when KAR is used as dispersion media instead of lubricant, the specific surface area increases due to the high density and viscosity of the media.

### 3.5. Hydro-transfer ability measurement

After hydroprocessing reaction, the products is analyzed by GC. The ratio that the ANT converted into DHA is obtained from the products GC, as shown in Table 5. The addition of  $\text{NH}_4\text{Cl}$  as the auxiliary agent for sulfurization promotes the hydro-transfer ability of the reaction system, so  $\text{NH}_4\text{Cl}$  plays an important role in the reaction system.

Also, the water-soluble sulfurization method and the thermal sulfurization has been compared in the sulfides' hydro-transfer ability, and results are shown in Table 6. It shows that the former is somewhat superior to the latter, which is commonly used.

Table 6  
Comparison of hydrogen-transfer ability of the sulfurization products for thermal-sulfurization method and water-soluble method

The way employed in catalyst sulfurization reaction	The ratio that ANT has been converted into DHA, %
Unsulfurized	33.3
Thermal sulfurized <sup>a</sup>	39.7
Water-soluble sulfurized <sup>b</sup>	42.2

<sup>a</sup> Reaction condition: sulfurization is carried out using sulfur as sulfurizer under 340 °C and presence of hydrogen.

<sup>b</sup> Reaction condition: sulfurization is carried out using  $\text{Na}_2\text{S}$  as sulfurizer,  $\text{NH}_4\text{Cl}$  as auxiliary agent under 80 and presence of hydrogen.

#### 4. Conclusions

1. The sulfurization process of molybdate has been divided three stages which has been studied, respectively. XRD analysis shows that intermediate oxothiomoledate ( $D > 20$  nm) has been formed in the sulfurization of molybdate. The final sulfurization product of molybdate is mainly made up of  $\text{MoS}_2$ , which has been analyzed by XRD, XPS, TEM and BET.
2. The instrumental analysis shows that  $\text{NH}_4^+$  is necessary for the sulfurization of molybdate. When the quantity of  $\text{NH}_4^+$  in the system increases, XRD analysis shows the crystallite size of the sulfurization products decreases from 6.6 to 3.6 nm, BET data show that its specific surface area increases from 55.6 to 61.7  $\text{m}^2/\text{g}$ , XPS analysis shows that S/Mo mole ratio on the surface does not change obviously while the proportion of MoIV species increases from 71% to 87%, and the total sulfurization ratio increases from 85% to 92%.
3. TEM analysis shows that the viscosity of dispersion media affects the sulfurization greatly. When sulfurized using KAR as dispersion media, molybdate obtains larger specific surface area, lower crystallite size and higher particle size than when sulfurized using lubricant as media.
4. The effect of water-soluble sulfurization method to promote the hydrogen-transfer ability of the catalysts notably excels that of the commonly used high-temperature method due to the special sulfurization mechanic of molybdate.

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