

Molybdenum Dialkyldithiophosphate as self-sulfurized catalyst precursor in Hydrocracking of Residue

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Abstract. The molybdenum dialkyldithiophosphate (MoDTP) with the feature of self-sulfurization, has been prepared, characterized and evaluated in the slurry-phase hydrocracking of Karamay atmospheric residue (KAR) as catalyst precursor. The self-sulfurization of MoDTP achieved fine MoS₂ particles with lower crystallinity and higher surface Mo⁴⁺ proportion in contrast to that of molybdenum naphthenate, implying the well sulfurized statement of MoDTP. Low coke yield and large asphaltene aggregate size using MoDTP proved the favorable hydrogenation activity of self-sulfurized catalyst in hydrocracking of residue.

1. Introduction

Slurry-phase hydrocracking has exhibited great advantages for the upgrading of inferior feedstock oils rather than the traditional hydroconversion process, because of the highly dispersed catalytic phases generated from the decomposition of oil-soluble or water-soluble precursors [1, 2]. Dispersed catalyst precursors formed very fine hydrogenation active particles with high surface area, and were proved to act as the supporters of coke in slurry reactors, which makes it possible to achieve high conversion efficiency of residue with little coke yield [3].

The active phases for hydroconversion mainly belong to sulfurated transition metals among which MoS₂ is the most commonly used catalyst [4]. The thermal decomposition and sulfurization of molybdenum precursors are the popular method to yield sulfurized MoS₂ nanoparticles. Molybdenum naphthenate have been thoroughly investigated in numerous literature, possessing significant hydrogenation effectiveness, generally experimented as the standard oil-soluble molybdenum precursor [5]. Lots of molybdenum alicyclic or aliphatic organic acids and molybdenum organometallic complexes were synthesized, exhibiting good compatibility with the oil media and appreciable catalytic activity [6]. However, the application of most molybdenum compounds demanded abundant amount of sulfur source, bringing troublesome engineering problems in sulfurization process. Molybdenum dialkyldithiophosphate (MoDTP) was mainly reported as lubricant antiwear agent [7], which has the characteristics of spontaneously forming fine and regular MoS₂ particles at high temperature. The self-sulfurization features make this kind of oil-soluble molybdenum precursor containing intramolecular sulfur was prospective for hydro-upgrading of residue [8, 9]. Previous literature mainly concerned the variation of synthetic methods or organic



ligands for MoDTP preparation as lubricating oil additives, however, few researches were reported in the field of slurry-phase hydrocracking for residue.

In the present work, characteristics of active phases from the self-sulfurization of synthesized MoDTP were investigated by means of multiple research methods. The catalytic performance of MoDTP was compared with molybdenum naphthenate through the analysis of mitigating coke formation and stabilizing asphaltene aggregate size in slurry-phase hydrocracking of residue.

2. Experimental

2.1. Catalyst preparation and sulfurization

MoDTP was prepared through a procedure detailed in a previous study [10]. In brief, sodium molybdate ($\text{Na}_2\text{Mo}_2\text{O}_4$) was mixed with excess sulfuric acid to obtain the Mo source, and then reacted with phosphorodithioic derived from the reaction of phosphorus pentasulfide and multiple alkyl alcohols, in the presence of strongly acidic cationic exchange resin. The product was filtered off, washed and dried in a vacuum oven to obtain the MoDTP sample. The molybdenum content of prepared MoDTP was 8.82 wt%, and the sulfur content was 15.39 wt%. Molybdenum naphthenate (purity of 99 % and molybdenum content of 6.7 wt%, Aaladdin Industrial. Inc.) was applied as the comparative catalyst precursor.

Transparent wax oil was mixed with $500 \mu\text{g}\cdot\text{g}^{-1}$ Mo catalyst precursor (calculated by the molybdenum content, the same below), and 0.2 g additional sulfur was essential when using the molybdenum naphthenate, before adding into a autoclave. Then the autoclave was charged by hydrogen with a initial pressure of 7 MPa, heating to the aimed sulfurization temperature. After 1 h of self-sulfurization at 375 °C, the autoclave was rapidly cooled, and sulfurized particles were obtained through the separation of products with adequate toluene and the subsequent drying of toluene insoluble.

2.2. Hydrocracking test

Karamay atmospheric residue (KAR) was used as the feedstock for the catalytic activity test of Mo catalyst precursors. 150 g of KAR and $150 \mu\text{g}\cdot\text{g}^{-1}$ Mo catalyst precursor with sulfur or not were loaded into a autoclave, initially charged with 7 MPa of hydrogen. After 1h of maintenance at the sulfurization temperature, hydrocracking reactions were carried out at 430 °C for 1h. Liquid products were distilled to obtain the naphtha (<180 °C), diesel (180-360 °C), vacuum gas oil (VGO, 360-480 °C) and vacuum residue (VR, >480 °C). The total coke was the sum of toluene insoluble on the inner wall and agitator of autoclave and the toluene-insoluble of VR fraction. Saturate, aromatic, resin and asphaltene (SARA) composition was separated from AR product by heptane extraction and liquid chromatographic column [11].

2.3. Characterization

The crystalline structures of sulfurized catalysts were studied by X-ray diffraction (XRD, Rigaku D/Max-III A). The X-ray photoelectron spectroscopy (XPS) spectra were acquired by Kratos Axis Ultra DLD spectrometer. By XPSpeak, an XPS analysis software, the existing forms of molybdenum on the surface of sulfurized catalysts were computed. Small-angle X-ray scattering (SAXS) was carried out for the particle size measurement of asphaltene aggregates, by a small angle scattering station (1W2A) in the Institute of High Energy Physics, Beijing. Data were processed using the software FIT2D and calculated according to the method reported in literature [12].

3. Result and Discussion

XRD pattern of sulfurized product from the self-sulfurization of synthesized MoDTP at 375 °C were showed in Figure 1. Significant diffraction (002) peak and (100) peak of the MoS_2 crystal were found at the 2θ angles of 14.7 ° and 33.69 °, respectively, with low and diffuse shapes which proved poor crystallinity. XRD pattern of sulfurized molybdenum naphthenate at 375 °C was compared, and the

(002) peak of 14.11° , (100) peak of 33.33° , (103) peak of 39.51° and (110) peak of 58.72° derived from the MoS_2 crystal were clearly identified. The diffraction peaks of sulfurized molybdenum naphthenate were also dispersed but stronger than the self-sulfurized MoDTP. The deficiency of some characteristic peaks of MoS_2 crystal in the pattern of self-sulfurized MoDTP was attributed to the lattice defects during the self-sulfurization, and the fine nanoscale of formed MoS_2 crystals would lead to diffuse low peaks in XRD patterns.

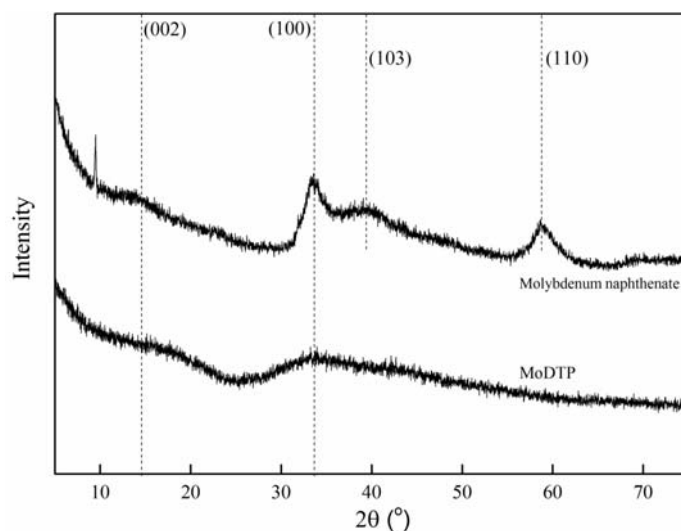


Figure 1. XRD patterns of sulfurized catalyst precursors.

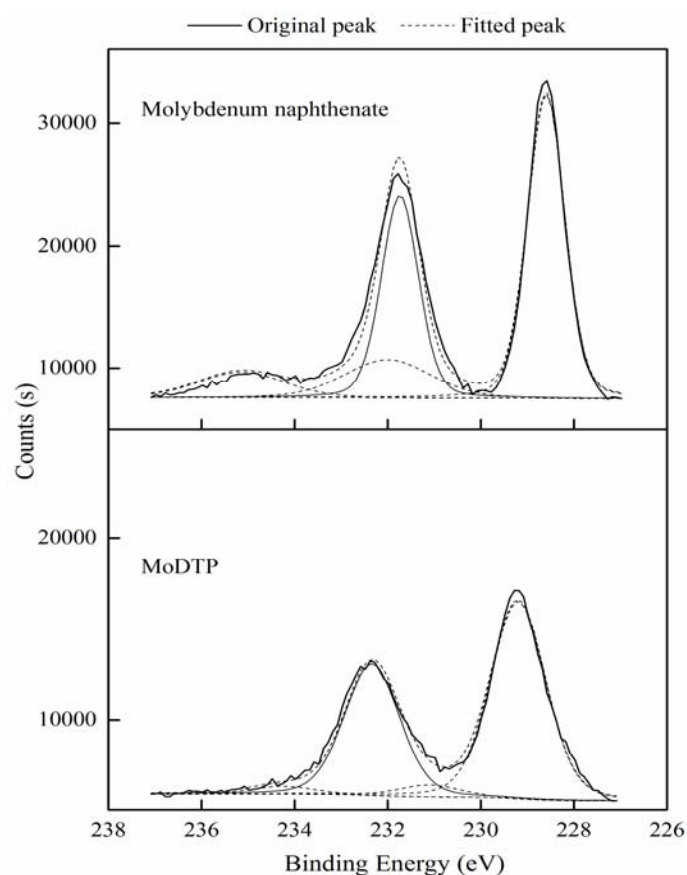


Figure 2. The $\text{Mo}3d$ XPS spectra of sulfurized catalyst precursors.

As for the molybdenum compounds, the hydrogenation catalytic activity of Mo^{4+} was considered far effective than the Mo^{6+} [13]. Thus, $x_{\text{Mo}^{4+}}$, the molar proportion of Mo^{4+} to the total molybdenum content, has a great positive correlation with the hydrogenation activity. The surface Mo^{4+} distribution of sulfurized MoDTP and molybdenum naphthenate were analyzed through the peak-differentiating and imitating of $\text{Mo}3d$ XPS spectra.

As demonstrated in Figure 2, the $\text{Mo}3d$ XPS spectra of sulfurized molybdenum naphthenate were fitted by considering two resolved doublets, namely the doublet of MoS_2 at 228.6~231.7 eV and the the doublet of MoO_3 at 232.0~235.1 eV. While the the inclusion of P into the system shifted the Mo^{4+} $3d_{5/2}$ peak maxima from 228.6 eV to 229.2 eV and was accompanied by a decrease in Mo^{6+} $3d_{5/2}$ peak maxima from 232.0 eV to 231.1 eV, demonstrating an interaction between P and Mo during the self-sulfurization of MoDTP. Further computed results from the XPSpeak software showed that the $x(\text{Mo}^{4+})$ of 93.66% on the surface of self-sulfurized MoDTP was far more than the $x(\text{Mo}^{4+})$ of 77.39% of sulfurized molybdenum naphthenate. The effective hydrogenation activity could be deduced from the highly dispersed statement and high surface $x(\text{Mo}^{4+})$ of self-sulfurized MoDTP.

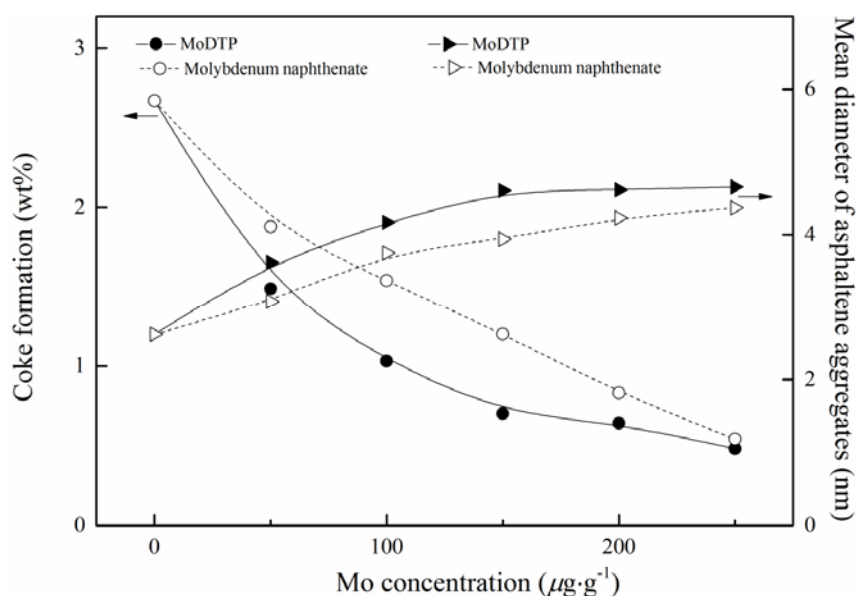


Figure 3. Coke formation and mean diameter of asphaltene aggregates from hydrocracking of KAR with different catalyst precursors.

Figure 3 showed the effect of synthesized MoDTP as well as molybdenum naphthenate for comparison, on the coke formation and mean diameter of asphaltene aggregates, after the slurry-phase hydrocracking of KAR. MoDTP had an excellent hydrogenation activity to decrease the total coke formation in contrast with the situation without catalyst, because of the enhancement to the formation of hydrogen radical which thus weaken excessive cracking and condensation reactions. Besides, the presence of fine MoS_2 particles would increase the nucleus quantity of coke formation and thus disperses the formed coke. As the increasing of Mo concentration from 0 to $250 \mu\text{g}\cdot\text{g}^{-1}$ using MoDTP, the amount of formed coke gradually decreased from 2.67 wt% to 0.48 wt%, with a sharper reducing trend and a lower coke yield compared with that of molybdenum naphthenate. And the mean diameter of asphaltene aggregates increased to 4.66 nm at the Mo concentration of $250 \mu\text{g}\cdot\text{g}^{-1}$ for the MoDTP after the hydrocracking, with a rise of 77.86 % compared to the reaction with no catalyst. The growth of asphaltene aggregate sizes should ascribe to the stabilization of sufficient activated hydrogen derived from the catalytic active sites to the asphaltene [15], which restrains the transformation of unstable asphaltene to coke at high temperature. In contrast, the increase extent of asphaltene

aggregate sizes was slightly lower using molybdenum naphthenate at the same Mo concentration, which further proved the better catalytic activity of MoDTP.

Table 1. Product distribution from hydrocracking of KAR with MoDTP.

Mo concentration ($\mu\text{g}\cdot\text{g}^{-1}$)	0	50	100	150	200	250
gas (wt%)	11.01	6.73	5.95	4.32	3.88	3.16
naphtha (wt%)	21.45	10.86	7.91	5.22	4.58	3.85
diesel (wt%)	19.82	30.74	28.37	26.12	24.25	22.93
VGO (wt%)	24.70	27.24	28.28	31.34	32.46	33.92
VR (wt%)	20.35	22.95	28.46	32.29	34.18	35.65
coke (wt%)	2.67	1.49	1.03	0.70	0.64	0.48
light oil (wt%)	41.27	41.59	36.28	31.34	28.83	26.79
<i>I</i> value	15.46	27.92	35.22	44.78	45.05	55.81

The product distribution from the slurry-phase hydrocracking of KAR with MoDTP was examined, as shown in Table 1. The addition of MoDTP decreased the thermal conversion of KAR and reduced the yield of light oil, deriving from the result of promoting the hydrogenation of hydrocarbon radicals. However, the light oil per coke ratio (*I* value) that means the weight ratio of light oil and coke, was more meaningful to describe the continuous running of slurry reactors. The obvious increase of *I* value with the increasing of Mo concentration, implying the excellent hydrogenation effect of synthesized MoDTP in the hydrocracking of residue.

4. Conclusion

The self-sulfurization of synthesized MoDTP could achieve fine particles of MoS_2 with lower crystallinity and higher surface Mo^{4+} proportion than the molybdenum naphthenate. During the slurry-phase hydrocracking of KAR, the self-sulfurized MoDTP showed better hydrogenation activity both in decreasing the coke yield and in stabilizing the remain asphaltene aggregates compared with the molybdenum naphthenate, thus exhibiting the potential to be novel dispersed catalysts in the application of hydrocracking for residue oil.

Acknowledgments

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