

Production of Clean Diesel Fuel by the Efficient Hydrotreating Technology

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Abstract: In this manuscript, an efficient unsupported Ni-Mo sulfide hydrotreating catalyst was prepared to produce the clean diesel fuel with ultra-low sulfur, nitrogen, and aromatics contents. The X-ray Diffraction (XRD), Low Temperature N₂ Adsorption (BET method), and High Resolution Transmission Electron Microscope (HRTEM) were employed to characterize the as-prepared catalysts. The characterization results indicate that the unsupported Ni-Mo hydrotreating catalyst has high specific surface area, large pore volume, and high MoS₂ stacking layers. The catalysts were evaluated in the micro-reactor using FCC diesel fuel as the raw material. The evaluation results reveal that the unsupported Ni-Mo catalyst has excellent hydrogenation performance.

Keywords: clean diesel fuel; hydrotreating technology; catalyst; hydrogenation

1. Introduction

Environmental concern has led to increasingly drastic regulations on sulfur, nitrogen and aromatics contents in diesel fuel. Indeed, heteroatom-containing and aromatics compounds present naturally in crude oil are sources of pollutants such as SO_x, NO_x or particulate matter (PM). In order to decrease the emission of off-gas pollutants, the production of clean diesel fuel with ultra-low sulfur, nitrogen and aromatics contents has become an urgent problem to be solved [1]. The most economical and effective measure to solve this problem is utilizing the efficient hydrotreating technology, especially using the catalysts with ultra-high hydrogenation performance. Previous studies have demonstrated that the unsupported hydrotreating catalysts have excellent hydrogenation performance because of no influence of the supports [2, 3]. However, previous unsupported catalysts are usually oxidation state, and must be presulfided before utilization. In the presulfidation process, the poisonous and odorous reagents must be used, which can lead to environmental pollution.

In this manuscript, an efficient unsupported Ni-Mo sulfide hydrotreating catalyst was prepared to produce the clean diesel fuel. Compared with the previous unsupported catalysts, this sulfide catalyst can be used directly without the presulfidation step. Meanwhile, the as-synthesized sulfide catalysts were characterized by X-ray Diffraction (XRD), Low temperature N₂ Adsorption (BET method), and High Resolution Transmission Electron Microscope (HRTEM) and were evaluated in the micro-reactor utilizing FCC diesel fuel as the raw material.

2. Experimental

2.1. Catalyst Preparation

Ammonium tetrathiomolybdate, elemental sulfur, and basic nickel carbonate were mixed and milled uniformly in a mortar according to an appropriate atomic ratio of Ni and Mo. Subsequently, the low temperature solid-state surface reaction was performed to the Ni-Mo-S mixture at 120°C for 24 hr under oxygen-free atmosphere, and then the mixture was decomposed thermally at 450~500°C for 3 hr in a tube furnace and the unsupported Ni-Mo sulfide hydrotreating catalyst could be obtained successfully.

One commercial Co-Mo-Ni-W/ γ -Al₂O₃ catalyst was selected as the compared catalyst, which had the active components of 32.47wt% and was presulfided before the activity evaluation.

2.2. Catalyst Characterization

X-ray diffraction (XRD) determination was carried out in a Panalytical X' Pert Pro MPD diffractometer, equipped with a curved graphite monochromator, using Cu-K α radiation ($\lambda=1.54060$ Å) operating at 45 kV and 40 mA at a scanning rate of 5 degree per minute.

Low Temperature N₂ Adsorption (BET method) for the determinations of specific surface area was performed with a Micromeritics TriStar 3000 system by nitrogen adsorption at -196 °C using the BET isotherm. Samples were degassed under flowing argon at 300 °C for 5 hr before nitrogen adsorption. The pore-size distribution was obtained from the desorption isotherm following the BJH method.

High Resolution Transmission Electron Microscope (HRTEM) was utilized to study the catalyst structure morphology and the HRTEM micrographs were recorded on a JEM-2100 analytical microscope operated at 200 kV with a side entry tilt which provided instrument resolu-

tion over a continuous range of periodicities down to 0.3 nm.

2.3. Catalyst Evaluation

The hydrogenation activities of the catalysts were evaluated in the micro-reactor using FCC diesel fuel (sulfur content: 3670.3 $\mu\text{g/g}$; nitrogen content: 1056.1 $\mu\text{g/g}$; relative density: $d_4^{20} = 0.9209$; aniline point: 18.6 $^{\circ}\text{C}$) as the raw material. The unsupported Ni-Mo sulfide catalyst can be evaluated directly; however, the compared catalyst must be presulfided before utilization.

The experimental conditions are listed as follows:

The catalyst dosage is 5 mL;

The reaction temperature is 300 $^{\circ}\text{C}$, 320 $^{\circ}\text{C}$, and 340 $^{\circ}\text{C}$, respectively;

The hydrogen pressure is 4.0 MPa;

Liquid hourly space velocity (LHSV) is 2 h^{-1} ;

The volume ratio between hydrogen and oil is 500:1.

The products were collected and analyzed for the sulfur and nitrogen contents, density and aniline point.

3. Results and Discussion

3.1. XRD Pattern

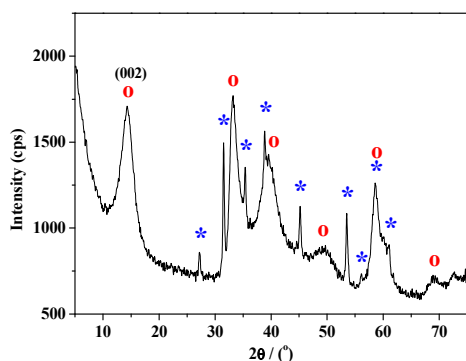


Fig.1. XRD pattern of unsupported Ni-Mo sulfide

*: NiS_2 O: MoS_2

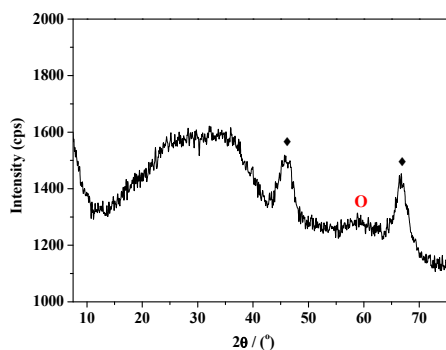


Fig.2. XRD pattern of the compared catalyst

◆: Al_2O_3 O: MoS_2

Fig. 1 and Fig. 2 present the XRD patterns of the unsupported Ni-Mo sulfide and compared catalysts, respectively. It can be seen from Fig. 1 that only the characteristic diffraction peaks of hexagonal 2H- MoS_2 and cubic NiS_2 appear and no oxides of Ni and Mo are detected, which indicate that the as-synthesized Ni-Mo sulfide catalyst is indeed a presulfided catalyst. The presence of a separate Ni sulfide phase is due to the high Ni contents used in the present study. The intensity of the (002) diffraction peak at $2\theta = 14^{\circ}$ is representative of the *c*-direction layer stacking of MoS_2 or WS_2 [4]. For the unsupported Ni-Mo sulfide catalyst, a quite strong (002) diffraction peak can be observed, which indicates that the *c*-direction layer stacking number of MoS_2 is very high. By comparison, the (002) diffraction peak is not detected in the compared catalyst (as shown in Fig. 2), which indicates that the *c*-direction layer stacking number of MoS_2 is very low. It was demonstrated in the previous studies [5] that the high MoS_2 or WS_2 layer stacking number was favor of the improvement of the hydrogenation performance. Accordingly, it can be speculated that the unsupported Ni-Mo sulfide catalyst should have excellent hydrogenation performance.

3.2. BET Characterization

The BET analysis results of the unsupported Ni-Mo sulfide and compared catalysts are listed in table 1. As shown in table 1, the unsupported Ni-Mo sulfide has the specific surface area of 162.5 m^2/g , pore volume of 0.54 cm^3/g , and the average pore diameter of 10.3 nm. By comparison, the compared catalyst has higher specific surface area of 180.9 m^2/g , however, the pore volume and average pore diameter is much lower, 0.29 cm^3/g and 5.0 nm, respectively. The larger pore volume and pore diameter is beneficial to the diffusion of the macromolecular compounds (e.g. dibenzothiophene) in the pore channel, which is favorable to enhance the catalytic activity.

Table 1. BET analysis results of the unsupported Ni-Mo sulfide and compared catalysts

Catalysts	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Unsupported Ni-Mo sulfide	162.5	0.54	10.3
Compared catalyst	180.9	0.29	5.0

3.3. HRTEM Micrograph

HRTEM micrographs observed at a magnification of 0.3 million for the unsupported Ni-Mo sulfide and compared catalysts are shown in Fig. 3 and Fig. 4, respectively. Typical MoS_2 layer-like structures could be recognized in Fig. 3 with the interlayer lattice fringe spacing of 0.61

nm and the bulk MoS_2 particles appear in closely packed groups of large slabs in highly folded shapes. The MoS_2 stacking layers are very high and different stacking layers cross with each other, and some stacking layers are bent. By comparison, the MoS_2 or WS_2 stacking layers are very low in the compared catalyst (as shown in Fig. 4). The HRTEM results are in agreement with the XRD results, that is, the unsupported Ni-Mo sulfide has much higher stacking number of MoS_2 layers.

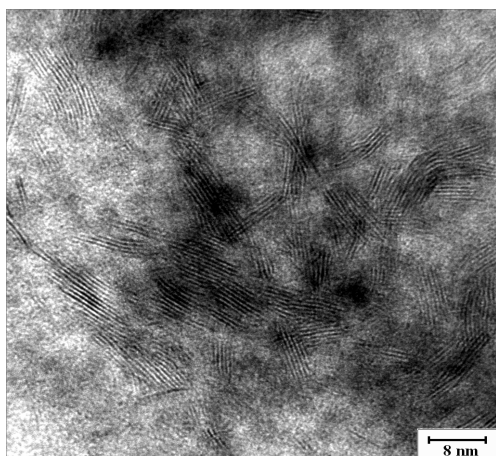


Fig. 3. HRTEM micrograph of unsupported Ni-Mo sulfide catalyst

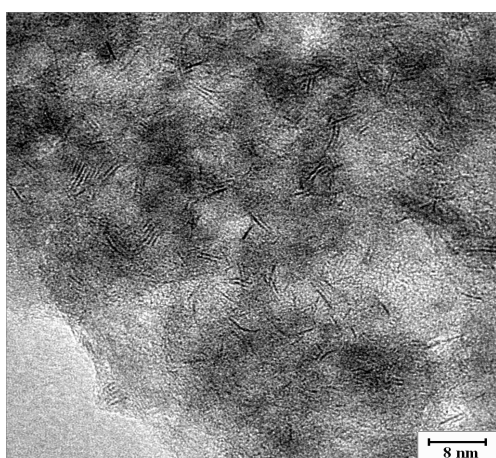


Fig. 4. HRTEM micrograph of the compared catalyst

3.4. Catalytic Activity Evaluation

The catalytic activity evaluation results for FCC diesel fuel of the unsupported Ni-Mo sulfide catalyst and compared catalyst are listed in table 2. It can be seen from table 2 that the desulfurization ratios and denitrogenation ratios of the unsupported Ni-Mo sulfide catalyst are all higher than those of the compared catalyst at 300 °C, 320 °C, and 340 °C, which indicates that unsupported Ni-Mo sulfide catalyst has excellent hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities. In addition, the denitrogenation ratios of unsupported Ni-Mo sulfide catalyst at 320 °C and 340 °C are all higher than the desulfurization ratios. This is a very interesting phenomenon, which is the most obvious difference between unsupported Ni-Mo sulfide catalyst and other catalysts. To the conventional catalysts, the HDS is relatively easy, and the HDN is difficult since the breakage of C-N bond is much difficult than C-S bond. On the other hand, according to the previous studies [6, 7], the HDN reaction is performed along a hydrogenation route, so the higher denitrogenation ratios mean the higher hydrogenation activity. Consequently, the excellent hydrogenation performance of unsupported Ni-Mo sulfide catalyst can be proved effectively by the ultrahigh HDN activity. In addition, the lower densities and higher aniline points of FCC diesel fuel produced by unsupported Ni-Mo sulfide catalyst also indicate the excellent hydrogenation performance of unsupported Ni-Mo sulfide catalyst. The activity evaluation results further confirm the XRD and HRTEM characterization results, that is, the unsupported Ni-Mo sulfide with higher stacking number of MoS_2 layers has much higher hydrogenation performance.

In addition, it can be seen that the desulfurization ratio is 98.2% and the denitrogenation ratio is 99.6% for unsupported Ni-Mo sulfide catalyst at 340 °C, and the density of FCC diesel fuel is decreased from 0.9209 to 0.8772, and the aniline point is increased from 18.6 °C to 28.2 °C. Consequently, the quality of FCC diesel fuel has been improved markedly, which demonstrates that the unsupported Ni-Mo sulfide catalyst is one kind of catalyst for producing clean and upgrading diesel fuel.

Table 2. Activity evaluation results of FCC diesel fuel for the catalysts

Reaction temperature (°C)	Desulfurization ratio (%)		Denitrogenation ratio (%)		Relative density (d_4^{20})		Aniline point (°C)	
	Unsupported Ni-Mo	Compared catalyst	Unsupported Ni-Mo	Compared catalyst	Unsupported Ni-Mo	Compared catalyst	Unsupported Ni-Mo	Compared catalyst
300	83.6	71.5	79.9	48.4	0.8885	0.8904	25.3	23.0
320	94.4	83.0	98.2	52.1	0.8820	0.8869	26.8	25.6
340	98.2	92.1	99.6	67.6	0.8772	0.8830	28.2	27.0

4. Conclusions

In this manuscript, an efficient unsupported Ni-Mo sulfide hydrotreating catalyst has been prepared successfully, which has high specific surface area, large pore volume, and high MoS₂ stacking layers. The activity evaluation results demonstrate that the unsupported Ni-Mo sulfide catalyst has excellent hydrogenation performance and can be used to produce clean and upgrading diesel fuel.

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