Heavy oil upgrading using magnetic molybdenum disulfide catalyst

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Abstract. In this work, the magnetic molybdenum disulfide catalyst ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MoS}_2$) was prepared and evaluated as a dispersed catalyst for the viscosity reduction of Canadian oil sand asphalt. The flower-like MoS$_2$ formed and some Fe$_3$O$_4@$SiO$_2$ particles were deposited on the surface of MoS$_2$. The catalytic reaction was carried out at 400°C and hydrogen pressure of 15 MPa. The results showed that the viscosity of the liquid product at 50°C dramatically decreased from 4660 mPa·s to 76.9 mPa·s and the degree of viscosity reduction reached 98%.

1. Introduction

Due to the global economic and population growth, the global energy demand has increased steadily. According to the projection of the International Energy Agency (IEA), the primary energy demand was predicted to increase by 1.5% per year. Although the government and society have vigorously developed new and renewable energy, fossil fuels represented 81% of the primary fuel in 2010 and are predicted to remain 75% in 2035 [1, 2]. But with the depletion of the conventional oil, it is important to exploit the unconventional oil, such as vacuum residue, heavy oils, tar sands. Owning to the low quality and high viscosity of the unconventional oil, it is hard to transport and process the oil [3].

At present, there are several technologies for the unconventional oil upgrading process: solvent de-asphalting, delayed coking, visbreaking, slurry phase hydrocracking [4]. Slurry hydroconversion process is very attractive due to the high conversion and less restrictions of the feed. MoS$_2$ are usually used as the catalysts in hydrocracking processes [5-8]. These studies had investigated the effects of the reaction parameters on the hydroconversion of heavy oil in detail. However, it is an important problem to recycle and reuse the dispersed catalyst during slurry hydroconversion processes. In recent years, the magnetic catalysts have received much attention due to the easy recovery of catalysts [9, 10]. So in this work, a kind of magnetic molybdenum disulfide catalyst ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MoS}_2$) was synthesized. The hydrocracking and viscosity reduction reactivity of the magnetic catalyst for the Canadian oil sand asphalt were studied.
2. Materials and methods

2.1. Materials

FeCl$_3$·6H$_2$O, sodium acetate, ethylene glycol, PEG6000, sodium hydroxide, tetraethyl orthosilicate (TEOS), ammonium hydroxide (28 wt.%), anhydrous ethanol, ammonium molybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O), thiourea, nickel sulfate hexahydrate were analytical reagent grade and used without further purification. Deionized water was used in all experiments.

2.2. Synthesis of magnetic molybdenum disulfide catalysts

2.2.1. Synthesis of magnetite Fe$_3$O$_4$ particles. The magnetite Fe$_3$O$_4$ particles were obtained via a solvothermal method reported previously with a slight modification [11]. Typically, FeCl$_3$·6H$_2$O (10.8 g) was dissolved in ethylene glycol (320 mL) to form a clear solution, followed by the addition of sodium acetate (14.4 g) and PEG6000 (8 g) sodium hydroxide (1.2 g). The mixture was stirred vigorously for 60 min at 45°C and heated in a 500 mL Teflon-lined stainless-steel autoclave at 200°C for 15 h. After cooling to room temperature, the black product was collected by the magnet, washed several times with ethanol and water.

2.2.2. Synthesis of silica-coated Fe$_3$O$_4$@SiO$_2$ microspheres. The Fe$_3$O$_4$@SiO$_2$ microspheres were prepared via the Stöber method with some modification [12]. The previous synthesized Fe$_3$O$_4$ particles were dispersed into a mixed solvent of 333 mL H$_2$O, 1 L ethanol, 16.8 mL ammonium hydroxide (28 wt.%) in a three-necked flask under continuous mechanical stirring. Then, TEOS (14 mL) was slowly added to this dispersion, and after stirring for 3 h, silica was formed on the surface of Fe$_3$O$_4$ particles through the sol-gel process. The Fe$_3$O$_4$@SiO$_2$ core-shell microspheres were also collected by the magnet, washed several times with ethanol and water, and then freeze-dried overnight.

2.2.3. Synthesis of magnetic Fe$_3$O$_4$@SiO$_2$@MoS$_2$ catalysts. The magnetic Fe$_3$O$_4$@SiO$_2$@MoS$_2$ catalysts were prepared through a hydrothermal reaction according to the previous method with some modifications [13]. Specially, Fe$_3$O$_4$@SiO$_2$ (1 g), (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (9.6 g), thiourea (22.8 g), nickel sulfate hexahydrate (1.4 g) were dispersed into 300 mL deionized water under vigorous stirring over 60 minutes. Afterwards, the solution was transferred into the 500 mL Teflon-lined stainless-steel autoclave at 180°C for 10 h. The obtained products were collected by a magnet and washed several times with the water and ethanol, and then freeze-dried overnight.

2.3. Catalytic tests

A 500 mL high-pressure and high-temperature batch-type autoclave reactor (Parr instrument, 4598 Micro Reactor) was used to study the hydroprocessing activities of the prepared magnetic catalysts. For this experiment, in order to conveniently weigh the crude oil, the crude oil was preheated in the oven for half an hour at 150°C. Then, the crude oil (170 g Canadian oil sand asphalt) was mixed with the Fe$_3$O$_4$@SiO$_2$@MoS$_2$ catalysts (0.17 g) and added into the reactor. The reactor was then sealed and purged with nitrogen to check for leakage. Afterwards, the reactor was pressurized to 15 MPa with hydrogen and heated to 400°C at 10°C/min with the stirring rate steadily increased to 1500 rpm. After reaction of 1.5 h, the autoclave was cooled to the room temperature and the liquid product was collected for analysis. The morphologies of the catalysts were characterized by scanning electron microscopy (SEM, JEOL JSM-6700F, Japan) and the viscosity of the liquid product was measured by the viscometer.

3. Results and discussion

The overall synthetic process of magnetic Fe$_3$O$_4$@SiO$_2$@MoS$_2$ catalysts involves three steps and it is schematically shown in Scheme 1: (1) solvothermal synthesis of Fe$_3$O$_4$ particles, (2) preparation of Fe$_3$O$_4$@SiO$_2$ microspheres via the Stöber method, and (3) hydrothermal synthesis of
Fe₃O₄@SiO₂@MoS₂ catalysts, while the detailed process is described in the previous synthetic methods.

**Scheme 1.** Schematic representation of the synthesis of Fe₃O₄@SiO₂@MoS₂ composites.

**Figure 1.** SEM images of as-prepared products. (a, b) Fe₃O₄; (c, d) Fe₃O₄@SiO₂.

Scanning electron microscopy (SEM) images of the Fe₃O₄ and Fe₃O₄@SiO₂ were shown in Figure 1. The Fe₃O₄ particles exhibited uniform size distribution of ca. 250 nm (Figure 1 (a, b)). Fe₃O₄ particles were used as catalysts support for the facile recovery. Meanwhile the stability of magnetic particles is a key factor to practical applications. In order to protect the support, the Fe₃O₄ were coated with thin SiO₂ layer. After SiO₂ coating, the size of Fe₃O₄@SiO₂ showed no obvious change compared with the pure Fe₃O₄ particles (Figure 1 (c, d)). The pure MoS₂ was synthesized using (NH₄)₆Mo₇O₂₄·4H₂O and thiourea via hydrothermal method. The flower-like pure MoS₂ showed obvious ripples and corrugations (Figure 2 (a, b)). The Fe₃O₄@SiO₂@MoS₂ composites were prepared
like the pure MoS₂ with the extra addition of Fe₃O₄@SiO₂. The flower-like MoS₂ formed and some Fe₃O₄@SiO₂ particles were deposited on the surface of MoS₂ (Figure 2. (c, d)).

![SEM images of the products. (a, b) MoS₂; (c, d) Fe₃O₄@SiO₂@MoS₂.](image)

The properties of the reactants are presented in Table 1. The Canadian oil sand asphalt is complex, extremely viscous in nature, and contains many impurities. These impurities include nickel, iron, vanadium, calcium, and compounds of sulphur, nitrogen, oxygen. In order to reduce the viscosity and ensure the transportation of the oil, catalytic hydrocracking experiment was conducted. The relationship between viscosity and temperature of the oil was presented in Figure 3. Before upgrading, the viscosity of Canadian oil sand asphalt was so high that it was difficult to transport the oil. The viscosity of Canadian oil sand asphalt was 4660 mPa·s at 50°C and it was reduced to 76.9 mPa·s after reaction. The degree of viscosity reduction reached 98%. The results demonstrated that the prepared magnetic catalysts had excellent catalytic activity. The recovery of the catalysts is a vital target in hydrocracking processes. In this experiment, the viscosity of the products had been significantly reduced compared with the crude oil. But, the viscosity was a little high when it was compared with the water. So in order to reuse the catalysts, we need build particular magnetic separator to realize the goal. The magnetic separator and recovery of the catalysts are under investigation.
Table 1. The main specification of the Canadian oil sand asphalt.

| Specification                          | Value   |
|----------------------------------------|---------|
| Density @15°C                          | 0.9364  |
| API Gravity                            | 19.5    |
| Ash                                    | 0.039   |
| Asphaltenes                            | 10.1    |
| Carbon Content                         | 83.5    |
| Hydrogen Content                       | 11.3    |
| Carbon Residue - Micro                 | 11.1    |
| Flash Point                            | <23.0   |
| Kinematic Viscosity@60°C               | 65.72   |
| Mercury Content                        | 9.82    |
| Arsenic                                | 111     |
| Metal - Nickel                         | 60      |
| Metal - Vanadium                       | 160     |

Figure 3. Relationship between viscosity and temperature of the crude oil.

4. Conclusions
In this study, the preparation of Fe₃O₄@SiO₂@MoS₂ was discussed. And it was used as a catalyst to reduce the viscosity of the Canadian oil sand asphalt. The result showed that the viscosity of the liquid
product which was measured at 50 °C reduced from 4660 mPa·s to 76.9 mPa·s and the degree of viscosity reduction reached 98%. The recovery method of the magnetic catalyst, magnetic separation device and the detailed characterization of the reaction products are also under investigation.

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