Catalytic activity of WS_2 nanoparticles in the hydrotreatment reaction on extra-heavy oil

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Introduction

The major industrial use of metal sulfides is in the removal of sulfur, nitrogen, metal atoms and hydrocracking from extra-heavy oil fractions by reductive treatments in so-called hydrotreating processes. Such processes are of paramount importance, because oil products must be purified to diminish air-polluting emissions of sulfur and nitrogen oxide. Furthermore, most catalysts that are used for the upgrading of oil streams in a refinery must therefore be hydrotreated. As a consequence, hydrotreating is the largest application of industrial catalysis on the basis of the amount of material (oil fractions) processed per year[1].

Hydrotreatment reaction is catalytic processes that involve Mo or W based catalysts, often doped with other transition metals. We synthesized WS_2 nanoparticles and used them as catalysts for the hydrotreatment reaction on extra-heavy oil in a batch reactor. To identity the physical and chemical properties of catalysts, various characterization techniques were applied, including transmission electron microscope (TEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET).

Materials and Methods

Synthesis of the WS_2 nanoparticles was carried out as follow two steps. First step, the mixture of W(CO)6 (Stream, 99%; 0.70 g), Me3NO·2H2O (1.33 g, Aldrich, 98%), and oleylamine (8.5 g, Aldrich, 70% (technical grade)) in a 100-mL three-neck round-bottom, connected to a gas bubbler, was slowly heated up to 553 K at a controlled rate of 4.6 K/min under inert atmosphere. A reflux condenser was used to prevent any loss of oleylamine due to evaporation. The reaction mixture became viscous, and allowed to stir at the same temperature for additional 12 hr. Second steps, Tungsten oxide nanorods (40mg) and hexadecylamine (1.45 g, 6mmol) were placed in a 100-mL three-neck round-bottom under inert atmosphere. The mixture was heated up to 523 K at a controlled rate of 2.8 K/min and carbon disulfide (0.12 mL, 2 mmol) was added into the tungsten oxide colloidal solution, and then subsequently heated to 603 K. The solution turned to black. After cooing the solution, the particles were separated by adding alcohol and centrifuging at 15,000 rpm for 30 min[2].

Results and Discussion

The structure of the product was examined with transmission electron microscopy. A WS_2 nanosheets are observed as shown in figure 1.

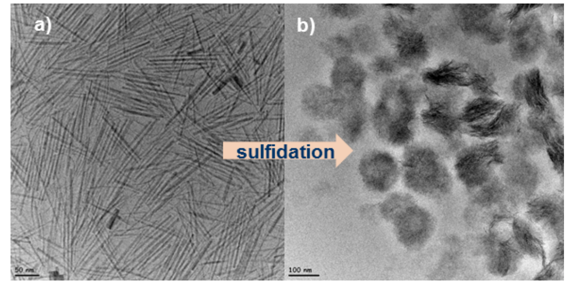

Figure 1. TEM images of WS_2 nanosheet crystals obtained by shape transformation of tungsten nanorods. Nanosheet crystals of about 90 nm in length (b) are obtained from tungsten oxide nanorods (a).

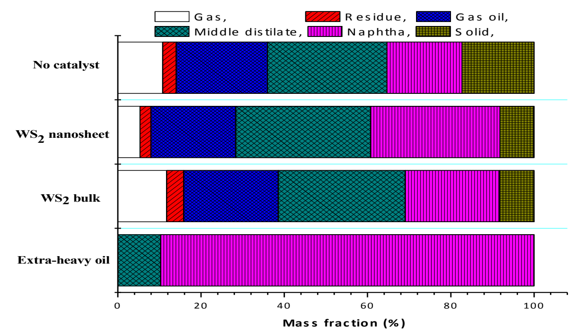

Figure 2 shows the mass fractions (or yields) of gas, liquid and solid (coke) inside the reaction after 4 h reaction using WS_2 catalyst. The liquid phase is again classified as naphtha, middle distillate, gas oil and residue based on the SIMDIS analysis results. In the absence of catalyst, the liquid products were only 72.1 wt.%, and gas and solid products were 11.3 and 16.6 wt.% respectively. However, when the applying WS_2 nanoparticle, the liquid products were increased with the decrease of gas and solid products.

Figure 2. The products yields of gas, liquid and solid products and the distribution of liquid products (naphtha, middle distillate, gas oil, and residue) was based on SIMDIS results.

Significance

The results of this work confirm the applicability of the WS_2 nanosheet catalyst in hydrotreatment reactions of extra-heavy oil**.** And the prepared WS_2 nanosheet catalyst showed excellent performance compared to the WS2 bulk catalyst

References

1. Matthias, B.; Albert, R.; Rutger, A. Catalysis; Wiley-VCH: Weinheim, 2012
2. Seo, J.-W.; Jun Y-W.; Park S.-W.; Nah, H.; Moon, T.; Park, B.; Kim, J.-G.; Kim, Y.- J.; Chen, J. W. *Angewandte Chemie* **2007**, 46, 8828