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Hydrocracking of vacuum residue into lighter fuel oils using nanosheet-structured WS_2 catalyst

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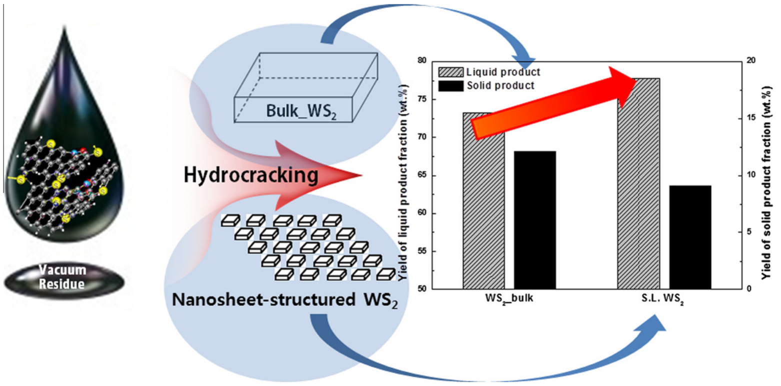
HIGHLIGHTS

- A WS_2 nanosheet was used as a catalyst in the hydrocracking of vacuum residue.
- The WS_2 nanosheet was applied as a dispersed colloidal catalyst in a batch reactor.
- The S.L. WS_2 catalyst exhibited the best hydrocracking activity.
- The yield of commercial liquid fuels increased with the use of the S.L. catalyst.
- Improvement in the API gravity and metal removal activity was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we tried hydrocracking of vacuum residue into lighter liquid oils using dispersed colloidal catalysts composed of nanosheet-structured WS_2 materials. The vacuum residue of API gravity = 2.3° was used as a reactant and hydrocracking reactions were performed in an autoclave batch reactor under 400 °C and the initial H_2 pressure of 70 bar. Both single and multi-layer WS_2 nanosheet catalysts were tested and their activities were compared with those of bulk WS_2 and MoS_2 catalysts. The single-layer WS_2, which was the highest in specific surface area (97.6 m^2/g) due to its smallest particle size, showed the best performances in commercial fuel fraction yield (45.4 wt.%), C_5-asphaltene conversion (75.3%), API gravity of liquid product (13.8°), and metal removal activity. To characterize the physicochemical properties of catalyst, various characterization techniques were applied, including transmission electron microscope (TEM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) analysis. In addition, to assess the qualities of hydrocracking products, we carried out API gravity measurement, inductively coupled plasma-mass spectrometry (ICP-MS), and simulated distillation (SIMDIS) analysis.

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1. Introduction

In spite of intensive efforts to develop and distribute alternative or renewable energy for many years, it is predicted that the dependence of world energy supply on fossil fuel resources will continue over the next several decades. The industry forecast that the oil energy will account for 30% of the global energy needs in 2030 [1]. The problem is the demand for petroleum products continuously increases although the reserves of sweet crude oil are close to depletion. As a solution, the industry is striving to find an efficient method to obtain commercial liquid oils from the low-quality petroleum resources such as vacuum residue, extra-heavy oil, natural bitumen, and oil sands. It is forecast that extra-heavy oil and oil sands will contribute to about 7% of the liquid oil supply in 2030 [1]. In addition, there is an industrial need that the residue oil fractions, which are the lowest in commercial value among the distillation products, has to be valorized as a feedstock for the lighter liquid oil products [2]. Among the residue oil fractions, vacuum residue (VR) is the heaviest one, which is obtained from the bottom of the vacuum distillation column (3.3–13.3 kPa, atmospheric equivalent b.p. $\geqslant$535 °C) [3]. VR is characterized by a high density (>0.9 g/cm^3 [4]), high molecular weight (967–2067 g/mol [4]), and an extremely high viscosity (1550–66,200 cP @ 100 °C [4]), for which it is frequently taken as a model reactant in the studies for upgrading extra-heavy oils [3–6]. VR contains high portion of asphaltanes, which are the most complex, heavy aromatic species containing high concentrations of impurities such as sulfur, nitrogen, oxygen, and heavy metals (vanadium, nickel, and iron) [7]. Those impurities are removed by hydrogenation during hydrocracking reaction. Therefore, for a heavy-oil-upgrading process, it is important to apply a hydrotreating catalyst which is capable of converting the asphaltene species into lighter liquid hydrocarbons containing minor impurities [8].

In the conventional oil refinery processes, the hydrocracking catalysts are typically composed of metal-supported acidic oxide catalysts. The sulfide of molybdenum or tungsten is frequently used as the active metal species in the commercial hydrocracking catalysts, because they exhibited overall good hydrotreating activities in hydrocracking, hydrodesulfurization, and hydrodemetallation [9,10]. The molybdenum or tungsten sulfide is usually supported (with Ni or Co as a promoting component) on one of the acidic support materials such as alumina and silica–alumina [11–13]. A critical problem of these supported catalysts is a short life time, which is caused by the deactivation by sulfur or coke deposition [14]. To overcome the problems associated with the use of supported catalysts, unsupported catalysts, which are dispersed in colloidal state over oil phase, are applied in hydrocracking of extra-heavy oils. Our group previously published a paper using Cs-exchanged phosphotungstic acids ($Cs_xH_{3-x}W_{12}O_{40}$, $x = 1$–3) as a unsupported, dispersed catalyst for hydrocracking of VR [15]. Many papers have claimed the advantages of using dispersed catalyst (slurry or colloidal catalyst) in hydrocracking of heavy oils [14,16]. The major advantages of dispersed catalyst are the reduction of coke formation and the enhanced removal of impuritic heteroatoms. Furthermore, the hydrocracking activity is substantially improved as the degree of dispersion increases. Several types of dispersed catalysts including oil-soluble metal (vanadium sulfide [17], molybdenum naphthenate [18], nickel carboxylate [19], nickel acetylacetonate [19], iron pentacarbonyl [20], molybdenum 2-ethyl hexanoate [20], molybdenum dithiocarboxylate [21], nickel naphthenate [21], and iron naphthenate [21]), and unsupported metal particles (molybdenum disulfide [22], nickel sulfide [23], cobalt sulfide [22,24], cobalt–molybdenum-sulfide [25], nickel–molybdenum-sulfide [23], and nickel–tungsten-sulfide [26]) have been developed for hydrocracking of heavy oils. Among the metal catalysts for hydrocracking, most studies about hydrocracking catalysts were obtained through extensive studies of molybdenum-based catalyst, but tungsten-based catalysts has been received less attentions [27] in spite of their competitive hydrocracking activities [28–30].

Recently, metal nanoparticles are widely used in catalytic applications [31,32]. The enhanced catalytic activity of nanoparticles basically relies on the increase of surface area to volume ratio. However, the nano-size effects (in size, shape, and crystal structure) bring striking changes in the chemical and catalytic properties of a material, which resulted in the unique and improved activities in various catalytic applications [12,33–37]. In this study, we used nanosheet-structured WS_2 as a dispersed catalyst for hydrocracking of vacuum residue. Two-dimensional, nanosheet-structured WS_2 particles were prepared by sulfiding the tungsten oxide nanorods which were obtained via decarboxylation of tungsten hexacarbonyl in a dispersed state over oleylamine surfactants [38,39]. The resulted products were single or multi-layer WS_2 nanosheets according to the length of sulfidation time, and both nanosheet materials can be easily redispersed over various kinds of organic solvents [38]. It was highly anticipated that the nanoscale particle size, high degree of dispersion over organic media, and enhanced open-edge morphology of the WS_2 nanosheet particles [38] would result in an enhanced activity in hydrocracking of extra-heavy oils. As far as we know, it was the first attempt to use the WS_2 nanosheet particles as a dispersed catalyst for hydrocracking of heavy oils. We evaluated the activities of WS_2 nanosheet catalysts diversely in commercial fuel fraction yield, C_5-asphaltene conversion, API gravity of liquid product, and metal removal activity. The activities of both single and multi-layer catalysts were evaluated, which were compared with those of conventional metal sulfide catalysts such as bulk WS_2 and MoS_2 catalysts.

2. Experimental

2.1. Preparation of nanostructured tungsten oxide and tungsten disulfide

The synthesis of two-dimensional WS_2 nanosheet crystals was based on the method of Seo et al. [38]. The method consisted of two-steps: (1) the synthesis of tungsten oxide ($W_{18}O_{49}$) nanorods [39] and (2) the shape-transforming sulfidation of the tungsten oxide nanorods into two-dimensional tungsten disulfide nanosheet [38].

First, the synthesis of tungsten oxide nanorods was as follows: The mixture of $W(CO)_6$ (Stream, 99%; 0.70 g), trimethylamine *N*-oxide (Aldrich, 98%; 1.33 g), and oleylamine (Aldrich, 70% (technical grade); 8.5 g) in a 100-mL three-neck round-bottom flask was slowly heated up to 280 °C at a ramp rate of 4.6 °C/min under argon atmosphere. A reflux condenser (10 °C) was applied to prevent any evaporative loss of oleylamine during the synthesis. The reaction mixture became viscous, which was stirred for additional 12 h at the same temperature. After cooling to room temperature, toluene (20 mL) and ethanol (50 mL) were added in order to precipitate tungsten oxide nanorods. The precipitates were separated with centrifugation at 15,000 rpm for 0.5 h, and then dried at room temperature.

Next, the nanosheet WS_2 crystals were synthesized from the as-prepared tungsten oxide nanorods: The tungsten oxide nanorods (40 mg) were redispersed in hexadecylamine (Aldrich, 90%; 1.45 g) at 250 °C under argon atmosphere. Then, carbon disulfide (Aldrich, anhydrous, +99%; 0.12 mL) was added with elevating the temperature to 330 °C. The color of slurry was turned to black, indicating the formation WS_2 nanosheet crystals. The single-layer WS_2 and multi-layer WS_2 (2–6 layers) were achieved as the sulfidation was continued for 0.5 and 1 h, respectively. (It will be

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