Fuel 185 (2016) 794–803

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Hydrocracking of vacuum residue using NiWS(*x*) dispersed catalysts

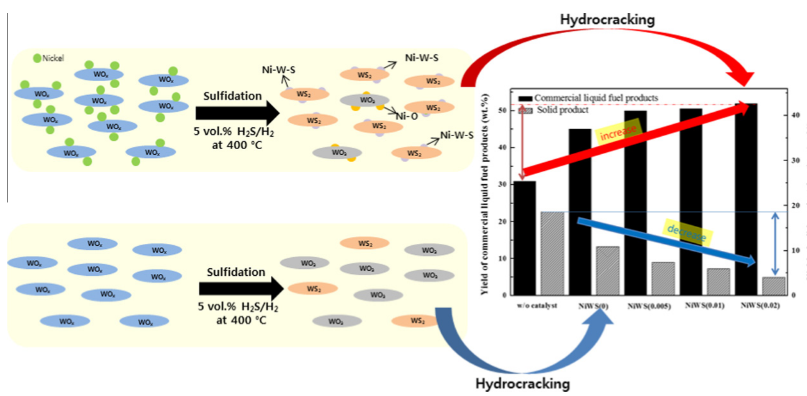
Young Gul Hur [a], Dae-Won Lee [b,*], Kwan-Young Lee [a,c,d,*]

[a] Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea
[b] Department of Chemical Engineering, Kangwon National University, 1, Kanwondaehak-gil, Chuncheon-si, Gangwon-do 24341, Republic of Korea
[c] Green School, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea
[d] KU-KIST Graduate School of Converging Science and Technology, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

HIGHLIGHTS

- NiWS(*x*) particles were used as a dispersed catalyst in the hydrocracking of VR.
- The activity of the NiWS(*x*) catalyst was strongly affected by the Ni content.
- NiWS(0.02) exhibited the best hydrocracking activity.
- The NiWS(0.02) catalyst produced a lighter oil than commercial catalysts.
- There were improvements in the API gravity and sulfur removal conversion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 March 2016
Received in revised form 1 August 2016
Accepted 2 August 2016

Keywords:
Vacuum residue
Hydrotreating
Hydrocracking
Dispersed catalyst
Ni-W-S catalyst

ABSTRACT

In this study, unsupported nickel-tungsten sulfide (NiWS(*x*)) particles, where *x* is the actual molar ratio of Ni/W (*x* = 0, 0.005, 0.01, 0.02), were prepared, characterized with XRD, XPS, TEM, and EDX elemental mapping, and applied as a dispersed catalyst for upgrading of extra-heavy oil into good-quality liquid products. The hydrocracking reaction of vacuum residue (VR) was carried out at 400 °C with an initial H_2 pressure of 70 bar. It was found that an increase in the Ni content increases the degree of sulfidation of tungsten, promotes formation of Ni-W-S phases, and enhances the overall catalytic activity. Among the NiWS(*x*) dispersed catalysts, the NiWS(0.02) catalyst showed the highest performance in total liquid product yield (87.0 wt.%), commercial fuel fraction yield (51.9 wt.%), API gravity value of liquid product (14.3°), and sulfur removal conversion (86.5%). In addition, coke formation (4.0 wt.%) was efficiently suppressed, and the C_5-asphaltene conversion (81.8%) was significantly raised.

1. Introduction

The energy industry forecasts that world oil demand will grow by approximately 13.8% between 2013 and 2040 (International Energy Outlook, 2014 report) [1]. This growth in oil demand is ascribed to the development of non-OECD countries such as India, Brazil, Mexico, and China [1,2]. However, light and sweet crude oil reserves have reached their limits, and much effort has been spent on research to provide against the exhaustion of these resources. Low-quality, heavy petroleum resources such as natural bitumen, oil shale, tar sand, and VR are becoming more and more important as additional sources in meeting the demand for the commercial fuel and petrochemical feeds [2,3]. The production of liquid fuels

* Corresponding authors at: Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea.
E-mail addresses: stayheavy@kangwon.ac.kr (D.-W. Lee), kylee@korea.ac.kr (K.-Y. Lee).

http://dx.doi.org/10.1016/j.fuel.2016.08.027
0016-2361/

Table 1
Actual Ni/W content and abbreviated expressions for the prepared catalysts.

Catalyst (abbreviated expression)	Molar ratio of nickel to tungsten (Ni/W)[a]
w/o catalyst[b]	–
WS_2_Commercial	–
MoS_2_Commercial	–
NiWS(0)	–
NiWS(0.005)	0.0054
NiWS(0.01)	0.0103
NiWS(0.02)	0.0197

[a] Nickel to tungsten ratio determined by ICP-MS spectrometer.
[b] Without catalyst.

Table 2
Properties of the reactant (VR).

Property	Value
API gravity (°)	2.3
>525 °C fraction (wt.%)	89.6
C_5-Asphaltene (wt.%)	23.1
Elemental analysis (wt.%)	
C	83.6
H	10.8
N	0.7
S	4.8
C/H ratio	7.7
Ni (ppm)	42.1
V (ppm)	99.3

from unconventional resources such as VR, bitumen, kerogen, and oil sand is expected to account for approximately 16.2% of the entire liquid fuel supply by 2040 [2]. Among the extra-heavy oils, VR has the worst quality: it is procured from the bottom of the oil distillate column under pressures of 3.33–13.33 kPa [4]. Its poor quality characteristics include high density (higher than water) and extremely high viscosity [5]. Furthermore, it contains various impurities (sulfur, nitrogen, and metals) and a high portion of asphaltene [6].

In the conventional oil-refinery process, both hydrocracking and hydrogenation reactions take place during the heavy-oil upgrading process, and impurities (sulfur, nitrogen, and metals) can be eliminated by hydrogenation reactions [7]. Metal-supported catalysts are generally used for hydrocracking. Sulfides of molybdenum and tungsten have been used as metal active species, and Ni and Co have been used as promoting species components. Acidic materials such as alumina, alumino-silicates, modified activated carbon, and zeolites have also been used as support materials for hydrocracking in the heavy-oil upgrading processes [8–12]. These metal-supported catalysts exhibit good hydrotreating activities in hydrodemetallation (HDM), hydrodesulfurization (HDS), and hydrocracking reactions [13–15].

However, when metal-supported catalysts are applied to hydrocracking in the upgrading of "*extra-heavy*" oil, a critical problem of a short lifetime can result from deactivation of the active sites by coke or sulfur deposition [16,17]. To overcome this problem, many studies have reported the use of various dispersed catalysts such as oil-soluble metals [18,19] and unsupported metal particles

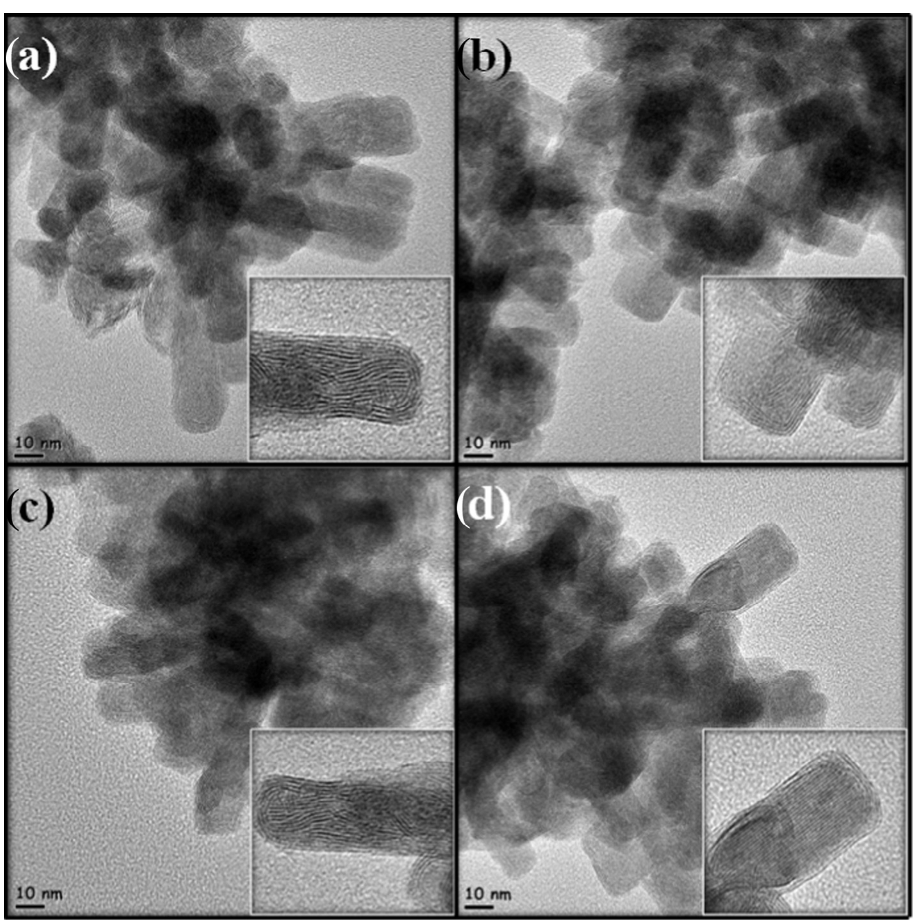


Fig. 1. TEM images of (a) NiWS(0), (b) NiWS(0.005), (c) NiWS(0.01), and (d) NiWS(0.02).