



Dispersion effects of Ni₂P catalysts on hydrotreating of light cycle oil



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ABSTRACT

A series of Ni₂P/SBA-15 catalysts with different Ni₂P loadings were prepared and applied for the hydrotreating of light cycle oil. The loading level of Ni₂P was varied from 0.5 to 3.0 mmol Ni₂P per 1.0 g of SBA-15 support, resulting in the optimum catalyst loading of 2.0 mmol Ni₂P. The physical properties of the catalyst samples were characterized by N₂-adsorption–desorption isotherms, CO uptake chemisorption, TPR, and TEM. X-ray diffraction (XRD) and extended X-ray absorption fine structure (XAFS) spectroscopy were used to obtain structural properties for the supported Ni₂P catalysts. Hydrotreating tests were performed in a continuous flow fixed-bed reactor at 623 K, 3.0 MPa, and LHSV's of 0.5–1.0 h⁻¹. The 2.0 mmol Ni₂P/SBA-15 gave an HDS conversion of 99.0% and an HDN conversion of 92.5%, which were much higher than those of a Ni–Mo–S/Al₂O₃ catalyst which gave an HDS conversion of 91.9% and an HDN conversion of 65.8% based on the same LHSV of 0.5 h⁻¹. Substantial changes in the composition of aromatic compounds were found for the Ni₂P/SBA-15 catalysts from 14.3 wt.% 1-Ar (mono-aromatics), 40.6 wt.% 2-Ar (di-aromatics) and 19.4 wt.% 3⁺-Ar (tri⁺-aromatics) in the LCO feed to 46.1 wt.% 1-Ar, 16.3 wt.% 2-Ar and 2.0 wt.% 3⁺-Ar in the product.

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1. Introduction

Light cycle oil (LCO) accounts for approximately 10–20 wt.% of the fluidized catalytic cracking (FCC) products and the stream has been used as low graded fuel additives due to its poor quality of low cetane number and high sulfur, nitrogen and aromatics contents [1]. In order to increase its use as a value-added diesel feedstock, a severe hydrotreatment is thus required [2–5]. Considering the high contents of heterocyclic compounds in LCO, the conventional hydrotreating catalysts may suffer from the competitive reactivity of hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodearomatization (HDA), and hydrocracking (HCK) [6–10]. The common hydrotreating catalysts are sulfided Co–Mo, Ni–Mo, and Ni–W. Co–Mo catalysts have higher HDS activity but with lower HDN and HDA activities than Ni–Mo and Ni–W catalysts [11]. One way to face these challenges is to develop alternative catalysts that can better withstand the severe operating conditions prevailed in the hydrotreatment process [12–15].

Recently, a new catalyst group of transition metal phosphides was introduced as a hydrotreating catalyst, which showed a good and stable catalytic activity for HDS and resistance to aromatic hydrocarbons and N-compounds [16,17]. Previous works have shown that MoP, WP, and Ni₂P have good activity in hydrotreating

[18–21]. Among the phosphides, nickel phosphide (Ni₂P) has been found to be the most active and stable in the HDS and HDN [16,22]. A study on the effect of the Ni₂P dispersion on the hydrotreating performance with a high surface area silica (350 m² g⁻¹) and a mesoporous siliceous material (790 m² g⁻¹) (MCM-41) as supports proved that Ni₂P catalysts supported on high surface area MCM-41 support exhibited better HDS activity for a refractory sulfur compound than a Ni₂P/SiO₂ catalyst at 613 K and 3.0 MPa based on equal sites (230 μmol) loaded in the reactor [23]. The use of high surface area supports provided an opportunity to investigate the effect of particle size or dispersion on the HDS and HDN activity, which demonstrated that the higher dispersion of Ni₂P catalyst gave the better catalytic activity for HDS and HDN [24].

Although much research has been made for the phosphide catalysts on the hydrotreating of diesel feedstocks, little work has been reported on the hydrotreating of LCO [17,25–29]. In the present study, we focused on preparing different loading levels of Ni₂P catalysts on high surface area SBA-15 support to examine the effect of Ni₂P dispersion on the hydrotreating of light cycle oil as a real feedstock.

2. Experimental

2.1. Synthesis of supported Ni₂P catalysts

Commercial SiO₂ supports (Cabot, Cab-O-Sil) was used as received. A mesoporous SBA-15 silica support was synthesized

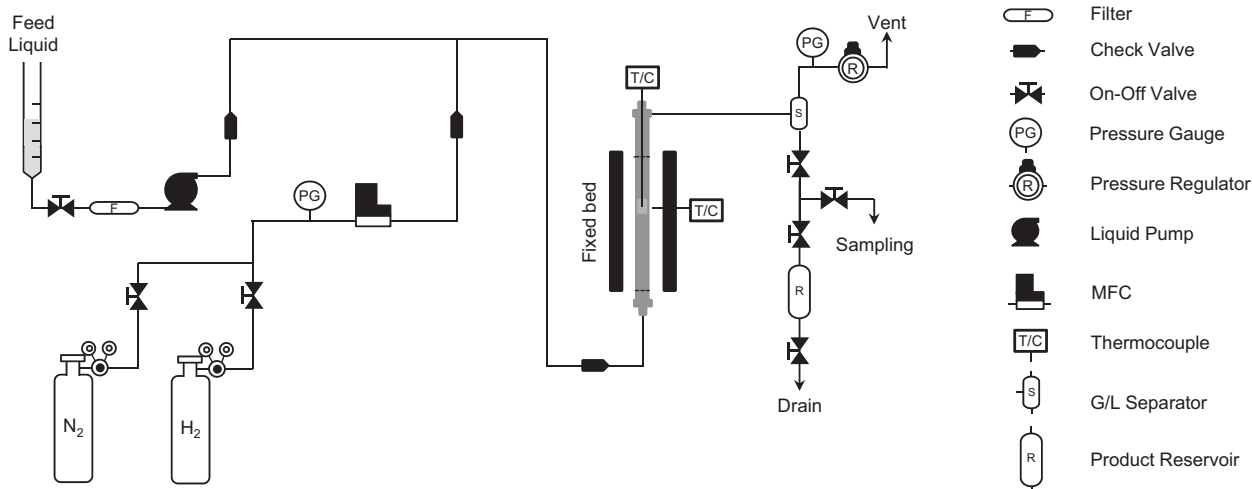
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by following a procedure in literature [30,31]. Supported Ni₂P catalysts were prepared by incipient wetness impregnation of aqueous metal phosphate precursors, followed by temperature programmed reduction (TPR) in flowing hydrogen. The initial Ni/P ratio in the precursors was fixed at 1/2. The amount of Ni loading was varied: 0.5, 1.0, 1.5, 2.0, and 3.0 mmol/g of support. The supported nickel phosphate precursor was prepared by incipient wetness impregnation of a solution of nickel nitrate, Ni(NO₃)₂·6H₂O (Alfa Aesar, 98%) and ammonium phosphate (NH₄)₂HPO₄ (Samchun, 99%), followed by drying at 393 K for 7 h and calcination at 673 K for 4 h. The resulting precursor phosphates were reduced to the corresponding phosphides by TPR from 298 to 873 K (at 1 K min⁻¹) in quartz U-tube reactors using hydrogen flow of 100 cm³ min⁻¹. After reduction, the phosphides were cooled to room temperature under 100 cm³ min⁻¹ helium flow and typically were passivated under 0.2% O₂/He flow (100 cm³ min⁻¹) for 4 h. For comparison, Co–Mo–S and Ni–Mo–S/Al₂O₃ catalysts were also prepared. The Ni–Mo/γ-Al₂O₃ and Co–Mo/γ-Al₂O₃ catalysts used in this work contained 10 wt.% Mo and 3 wt.% promoter (Ni or Co). They were prepared by incipient wetness impregnation of γ-Al₂O₃ (Alfa Aesar, 99.9%, metals basis) with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (Samchun, 99%), followed by an aqueous solution of Ni(NO₃)₂·6H₂O (Alfa Aesar, 98%) or Co(NO₃)₂·6H₂O (Kanto, 99.9%). After each impregnation step the catalysts were dried overnight at 393 K and calcined at 773 K for 2 h.

2.2. Characterization of catalyst samples

The temperature programmed reduction (TPR) technique was used to identify the reduction characteristics of the material. 0.20 g of material was loaded in a quartz glass U-tube reactor and the effluent was monitored by a mass spectrometer (HP 5973 inert). CO chemisorption uptake was measured on passivated samples reduced in situ in a H₂ flow (100 cm³ min⁻¹) at 723 K for 2 h before the measurements. Pulses (100 μmol) of CO at room temperature (300 K) were passed over the sample to measure the total dynamic gas uptake. A Micromeritics ASAP 2010 micropore size analyzer was used to measure the specific surface area of the sample from the linear portion of BET plots ($P/P_0 = 0.01–0.10$) at 77 K. TGA measurements were carried out on a SDT 2960 (TA instruments) and alumina pans. About 10 mg of each sample was equilibrated at 313 K for 5 min and then heated from 313 K to 1063 K with a heating rate of 10 K min⁻¹ under nitrogen atmosphere and nitrogen gas flow of 50 cm³ min⁻¹.



Scheme 1. Schematic of hydrotreating unit.

Table 1
Composition and properties of light cycle oil (LCO).

Physical properties	LCO	
API	13.5	
S/ppm	3930	
N/ppm	550	
Color (ASTM)	L2.5	
Aromatics/wt.%	Total	74.3
	Mono	14.3
	Di	40.6
	Tri	19.4
Cetane index	24.9	
Distillation/K	IBP/5/10	498/529/535
	30/40/50	557/565/581
	60/90/95	598/671/–
	EP	–

The chemical composition of the samples was determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) (PerkinElmer, Model Optima-4300 DV). HR-TEM images were obtained using a JEM-2100F, 200 kV microscope. X-ray absorption spectra at the Ni K-edge (8.333 keV) of the reference and catalyst samples were recorded in the energy range 8.233–9.283 keV using synchrotron radiation at the beamlines 7D and 10C of the Pohang Light Source (PLS). The X-ray ring at the PLS has a flux of 5×10^{12} photons s⁻¹ at 100 mA and 3 GeV. The X-ray single crystal at the beamline 10C is equipped with a Si (1 1 1) channel-cut monochromator and has an energy range capability of 4–22 keV. The samples were prepared in a kapton sealed glass cell to avoid air-exposure. The X-ray absorption spectra were recorded at ambient temperature in transmission mode using ionization chambers for the detection of primary (I_0 , 100% N₂) and transmitted (I_T , 100% N₂) beam intensities. The obtained XAFS data were analyzed by Winxas 3.1.

2.3. Activity test for hydrotreating of light cycle oil

The catalytic tests of hydrotreating were carried out in a continuous-flow reactor (catalyst loaded with 1.0 cm³) as displayed in [Scheme 1](#) at 3.0 MPa and 623 K. Before injecting the reactant, the catalysts were activated in situ under H₂ flow of 100 cm³ min⁻¹ (99.999%) at 723 K for 2 h to remove the oxygen from the surface. The sulfide catalysts were pretreated at 573 K for 2 h with 100 cm³ min⁻¹ of 10% DMDS/H₂ at 1 atm. Light cycle oil was supplied from a refinery in Korea. The specifications of the light cycle oil used in this study are summarized in [Table 1](#). The light

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