Morphology effect of β-zeolite supports for Ni₂P catalysts on the hydrocracking of polycyclic aromatic hydrocarbons to benzene, toluene, and xylene

Yong-Su Kim, Kye-Sung Cho, Yong-Kul Lee *

Laboratory of Advanced Catalysis for Energy and Environment, Department of Chemical Engineering, Dankook University, 152 Jukjeonro, Yongin 16890, South Korea

A B S T R A C T

Ni₂P catalysts supported on nano-sized β (β-N) or micrometer-sized β (β-M) zeolites were prepared by temperature-programmed reduction, and their structural and chemical properties were analyzed by N_2 physisorption, transmission electron microscopy, X-ray diffraction, extended X-ray absorption fine structure, NH_3 temperature-programmed desorption, and CO uptake. The catalytic activity was tested at 653 K and 6.0 MPa in a fixed bed reactor for the hydrocracking of 1-methylnaphthalene (1-MN) into benzene, toluene, and xylene (BTX). In the hydrocracking, Ni₂P/β-N showed better activity and stability for hydrocracking of 1-MN than Ni₂P/β-M, with BTX yields of 42.3% and 30.5% for Ni₂P/β-N and Ni₂P/β-M, respectively. In addition, Ni₂P/β-N maintained the stability in terms of catalytic activity and local structure, while Ni₂P/β-M suffered from coke formation, particularly in the presence of heavy aromatics such as phenanthrene in the feed. The characterization results demonstrated that the β-N has abundant inter-crystalline mesopores to provide better dispersion for Ni₂P catalysts and accessibility toward acid sites, offering the proximity of the hydrogenation active center and the cracking sites. Kinetic analysis for the hydrocracking of 1-MN over the catalysts revealed that the Ni₂P/β-N catalyst shows superior activity for both hydrogenation and cracking over the Ni₂P/β-M catalyst.

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1. Introduction

Light aromatic hydrocarbons are important sources for the petrochemical industry and have been highly in demand for the past decades [1–3]. Among these, benzene, toluene, and xylene (BTX) are important sources for the production of valuable polymers and special chemicals such as solvents, paints, polishes, and pharmaceuticals. Heavy oil fractions such as pyrolysis fuel oils from naphtha crackers and light cycle oils from fluidized catalytic crackers are rich in polycyclic aromatic hydrocarbons (PAHs) of naphthalene, anthracene, and phenanthrene derivatives, which can be converted into valuable light fuels or aromatics such as benzene, toluene, and xylene (BTX) [4,5]. Catalytic hydrocracking can be an effective option for converting PAHs into BTX via bifunctional catalysis, i.e., hydrocracking [6–9].

In catalytic hydrocracking, partial hydrogenation of the polyaromatic rings and cracking of the resulting naphthenic ring are key steps, in which bifunctional catalysts such as metals supported on acid catalysts have mostly been applied [8–16]. In this regard,

the effect of metal catalysts on the hydrocracking of two- or three-ring aromatic compounds and alkyl aromatic compounds has been investigated by a number of investigators [7–9,12,15–19]. Murzin et al. [20] proved that H-zeolites on which Pt is present enhance ring-opening rates for tetralin five times more than H-zeolites. Kubicka et al. [21], using various zeolites, suggested that the ring opening of decalin proceeds via ring contraction and the reaction rate reaches the optimum with a β zeolite exhibiting medium acidity. In the study, coke formation was attributed to more acidic zeolites such as mordenite. Similarly, Santikunaporn et al. [13] confirmed intermediate acidity as a key factor in the ring-opening selectivity for decalin and tetralin. Moreover, the use of large-pore zeolites favors the ring-opening reaction by limiting deactivation due to coke deposits [21–23].

As an alternative to using noble metals as active hydrogenation centers, conventional metal sulfides have shown activity in hydrocracking. Eliche-Quesada et al. showed that a NiW/Zr-MCM-41 catalyst is active for tetralin hydrocracking [24]. Upare et al. [25] reported CoMo/β hydrocracking catalysts for upgrading pyrolysis fuel oils that contain a mixture of heavier polyaromatic hydrocarbons (PAHs) such as naphthalene and alkyl naphthalene and obtained 43.3% of monocyclic aromatic hydrocarbons yield with

70% conversion of pyrolysis fuel oils. A new hydroprocessing catalyst group of transition metal phosphides has recently been introduced [26–29]. Among the metal phosphide catalysts, Ni_2P is known to show the best activity in hydrotreating [27–29]. Moreover, the Ni_2P catalysts have shown superior hydrogenation activity over sulfide catalysts, even in the presence of nitrogen compounds [29–32].

The studies of acid-catalyzed ring opening have been performed primarily on zeolites. Zeolites often exhibit superb cracking activity, but with fast deactivation, mainly due to poor diffusion efficiency as a result of coking in cracking reaction. Tarach et al. [33] suggested that cracking of gas oil over mesoporous β zeolite promoted cracking activity with high propylene selectivity. Kenmogne et al. [34], using a Pt/Al-MCM-48 catalyst, confirmed that a bifunctional catalyst with a mesoporous system promotes hydrocracking of heavy oils. Samad et al. [35], with varying ratios of metal to acid in Pt/SiO₂–Al₂O₃ catalysts, showed that optimal proximity between metal and acid sites for bifunctional behavior is achieved at the nanometer or micrometer scale. Nano-sized zeolites are therefore expected to be promising materials with low diffusion resistance as well as a large external surface area, which improves their catalytic activity. Similar behavior has recently been reported for nano-sized zeolites with sizes less than 20 nm, which have been receiving much attention, showing better catalytic and adsorptive properties than micrometer-sized ones because of efficient mass transport of molecules [32,36–39].

Although the catalytic hydrocracking of heavy oil fractions such as vacuum gas oil over conventional sulfide catalysts has been widely studied, research on the hydrocracking of refractory polycyclic aromatic hydrocarbons is still lacking. The goals of this work are thus to examine the effect of $Ni_2P/β$ as a new hydrocracking catalyst on the hydrocracking of 1-methylnaphthalene (1-MN) and phenanthrene and to explore the reaction mechanism of hydrocracking over Ni_2P catalysts supported on two different β zeolites: nano-sized β (β-N) or micrometer-sized β (β-M). Measurements were carried out at 653 K and 6.0 MPa H_2 in a fixed bed reactor using a model feed of 1-MN and phenanthrene. Moreover, structural properties of the fresh and spent catalysts were analyzed by EXAFS measurements.

2. Experimental

2.1. Synthesis of supported Ni_2P catalysts

The supports used in this study were two kinds of β zeolite having different crystal sizes: nano-sized β (CP814E, Zeolyst) and micrometer-sized β (HSZ-931HOA, Tosoh), denoted as β-N and β-M, respectively. The amount of Ni loading was fixed at 1.5 mmol g^{-1} of support with an initial P/Ni ratio of 2.0 in the precursors. The supported nickel phosphate precursor was prepared by incipient wetness impregnation of a solution of nickel nitrate $Ni(NO_3)_2 6H_2O$ (Alfa Aesar, 98%) and ammonium phosphate $(NH_4)_2HPO_4$ (Samchun, 99%), followed by drying at 373 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 5 K min^{-1}) in quartz U-tube reactors using 100 cm^3 min^{-1} H_2 flow. After reduction, the phosphides were cooled to room temperature under 100 cm^3 min^{-1} He flow followed by passivation under 0.1% O_2/He flow (100 cm^3 min^{-1}) for 4 h.

2.2. Characterization of catalyst samples

Temperature-programmed reduction (TPR) was used to identify the reduction characteristics of the material. A sample of 0.20 g was loaded into 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 re-reduced in situ under H_2 flow (100 cm^3 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. XRD patterns of the samples were characterized using a diffractometer (Rigaku DMAX-2500) operated at 60 kV and 300 mA with Cu Kα radiation ($λ$ = 0.15418 nm). Crystallite sizes were calculated from the XRD peaks using the Scherrer equation, $D_c = Kλ/β\cos(θ)$, where $λ$ is the wavelength of the X-ray radiation, $β$ is the peak width in radians at half-maximum, K is a constant taken as 0.9 corrected for instrumental broadening (0.1°), and $2θ$ is the Bragg angle of the reflection. N_2 adsorption–desorption isotherms of the sample were measured on a Micromeritics ASAP 2010 micropore size analyzer. The specific surface area was calculated by the linear portion of BET plots (P/P_0 = 0.01–0.10) at 77 K. The desorption branch of the isotherm was used to calculate the pore distribution according to the BJH method. The chemical composition of the samples was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Perkin–Elmer, Model Optima-4300 DV). High-resolution transmission electron microscope (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 beamline 8C of the Pohang Light Source (PLS). The X-ray ring at the PLS has a flux of 5×10^{12} photons s^{-1} at 200 mA and 3 GeV. The X-ray single crystal at beamline 8C is equipped with a Si (1 1 1) channel-cut monochromator with 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% N_2) and transmitted (I_T, 100% N_2) beam intensities. The obtained XAFS data were analyzed by Winxas 3.1. To fit the experimental EXAFS spectra for the fresh and spent samples, the theoretical EXAFS spectrum for Ni_2P was used to calculate phase shifts and amplitude functions of Ni_2P [40], using FEFF 8.0 code [41]. Fitting was then carried out for the fresh samples using the three dominant shells (2 Ni–P at 0.2266 nm, 4 Ni–P at 0.2457, and 4 Ni–Ni at 0.2678 nm), using a reducing factor (S_0^2) fixed as 0.70, a value obtained by fitting the Ni–Ni contribution in Ni foil.

The acidity of the prepared zeolites was characterized by the temperature-programmed desorption of ammonia (NH_3 TPD) in a chemisorption unit, equipped with a mass spectrometer (HP 5973 inert). The catalyst sample was loaded into a quartz glass U-tube reactor and preheated to 673 K (7 K/min) for 60 min under He flow before exposure to NH_3 at 373 K. The NH_3 TPD measurement was then conducted from 373 to 1073 K and from 313 to 1073 K at a heating rate of 10 K/min under a He flow of 100 cm^3 min^{-1}. The total acid sites were quantified from the NH_3 TPD profile based on the TPD peak area.

Infrared spectra of pyridine adsorbed onto the $Ni_2P/β$ samples were collected using a Fourier transform infrared spectrometer (Nicolet 8700, Thermo Scientific) equipped with a heatable in situ transmission cell with water-cooled KBr windows. The samples were pressed into self-supporting wafers with a diameter of 20 mm and a weight of 13 mg. IR spectra were collected in the absorbance mode at a resolution of 2 cm^{-1} in 64 scans in the region 4000–400 cm^{-1}. Studies of the effect of temperature were performed on these samples to determine the identity and stability of the adsorbed species on the catalyst surface. In situ FTIR measurements on $Ni_2P/β$ samples were made in a gas mixture of 5% H_2/He. The Ni_2P samples were pretreated in the 5%H_2/He flow at 723 K for 2 h. For the measurements of pyridine adsorption, the