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Selective hydrocracking of tetralin for light aromatic hydrocarbons

Jihye Lee, Yeseul Choi, Jaeuk Shin, Jung Kyoo Lee*

Department of Chemical Engineering, Dong-A University, Busan 604-714, Republic of Korea

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ABSTRACT

Hydrocracking (HYC) of tetralin was studied in a fixed-bed down-flow reactor under 4 MPa as a model reaction for polyaromatic hydrocarbons (PAHs) conversion to light aromatic hydrocarbons such as BTX and C_9 aromatics. HYC catalysts were prepared by supporting various metals, (Ni, Ni-Sn and CoMo-S) possessing different hydrogenation (HYD) activity, on H-Beta. HYC of tetralin over Ni/H-Beta catalysts with various Ni contents (1-10 wt%) resulted in a non-selective HYC behavior to give low BTX yield but high yields of gaseous and naphtha products due to strong HYD activity of Ni. The HYD activity of Ni was suppressed by forming Ni-Sn intermetallic compounds by Sn addition. Thus, Ni-Sn/H-Beta catalysts showed BTX and BTX+C_9A (C_9 aromatics) yields as high as 48.1 wt% and 53.1 wt%, respectively. The BTX and BTX+C_9A yields corresponded to about 75 and 83% of the theoretical yield, respectively. CoMo-S/H-Beta, whose metal showed the lowest HYD activity, also exhibited BTX (47.4 wt%) and BTX+C_9A (55.5 wt%) yields comparable to those obtained over Ni-Sn/H-Beta. Besides metallic function in HYC catalysts, H_2/tetralin molar ratio greater than 4 and H-Beta with a moderate acidity are desirable to achieve a highly selective HYC of tetralin into BTX with high yield at low hydrogen consumption.

1. Introduction

Polyaromatic hydrocarbons (PAHs) of diesel boiling point range are produced in large amount as process by-products in oil refining and petrochemical plants. Among them, light cycle oil (LCO) from fluidized catalytic cracker (FCC) is produced in the largest amount. Major compounds in LCO are condensed two- and three- aromatic ring hydrocarbons such as naphthalene, alkyl-naphthalenes, anthracenes and phenanthrenes etc. [1–3]. Sulfur and nitrogen contents in LCO are rather high [3]. Besides LCO, a substantial amount of PAHs is also produced from naphtha cracking centers (NCC) and para-xylene plants, which are pyrolysis fuel oil (PFO) and C_{10}^{+} heavy aromatics, respectively [4,5]. Sulfur and nitrogen contents in these fractions are very low compared to those in LCO [4]. Presently, these PAHs are used as a blending stock of heavy fuel oil for viscosity adjustment (mostly for LCO) or just burned as plant fuels [1,4,5]. A small portion of PFO is used as a swelling solvent in styrene-butadiene rubber (SBR) [4]. However, the demand of heavy fuel oil will be decreasing in the future due to environmental concerns. Furthermore, the disposal of PFO and C_{10}^{+} heavy aromatics as plant fuels is wasting resources from petroleum oil considering its very low level of impurities such as sulfur and nitrogen.

Therefore, it is highly demanding to upgrade these PAHs into high-value products. One of active approaches is upgrading PAHs into diesel blending stocks that have suitable qualities such as high cetane number, and low contents of total PAHs and total aromatic hydrocarbons [2,6–8]. Recently, PAHs conversion into light aromatic hydrocarbons such as benzene, toluene and xylenes (BTX) has attracted a great attention as an alternative approach, which can be more economic solution for PAHs upgrading [3,5,9–13]. In both approaches, it is desirable to develop catalytic solutions giving high yield of desired products (diesel blending stock of high quality or BTX) with hydrogen consumption as low as possible. Due to the extremely high contents of 2- and 3-ring aromatics in these PAHs, a two-step hydroconversion process consisted of hydrotreating and/or hydrogenation (HYD), and subsequent hydrocracking (HYC) could be considered for BTX production from PAHs [5,12]. In the first step, partial HYD of PAHs to 1-ring aromatic compounds containing naphthenic-rings occurs along with hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). Then, the naphthenic-rings in 1-ring aromatic compounds are hydrocracked to yield light aromatic hydrocarbons. Furthermore, huge exothermic heat and chemical equilibrium involved in the hydroconversion of PAHs [6] can be controlled in a more efficient manner in a two-step process than in a single-stage conversion process.

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* Corresponding author. Tel.:+82 51 200 7718; fax:+82 51 200 7728.
E-mail address: jklee88@dau.ac.kr (J.K. Lee).

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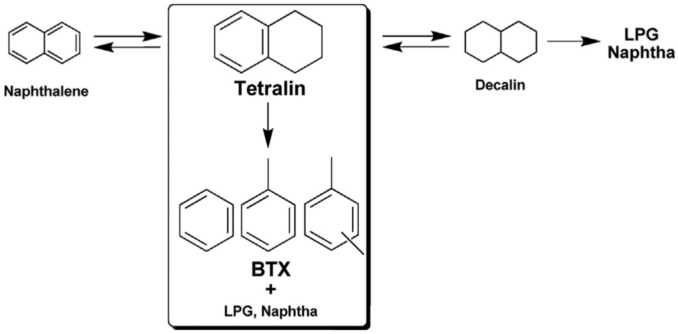

Scheme 1. Catalytic scheme for the selective hydrocracking of tetralin into BTX.

We depicted such a two-step process with naphthalene as a model reactant of PAHs in Scheme 1, in which one-ring of naphthalene is selectively hydrogenated into tetralin, and then tetralin is hydrocracked to yield BTX. Since naphthalene content is the largest in most PAHs, tetralin HYC shown in the scheme can serve as a model reaction to study HYC catalysts [5,11,14]. In the scheme, the HYC of tetralin into BTX in the box is the desired reaction. However, as side-reactions, tetralin can be dehydrogenated back into naphthalene or further hydrogenated into decalins, which are susceptible to cracking to yield gaseous product (LPG) and naphtha accompanied with additional hydrogen consumption. Therefore, the HYD power of metallic function of bifunctional HYC catalysts has to be properly controlled to avoid not only the excessive cracking of tetralin to low value LPG/naphtha but the additional hydrogen consumption. In most commercial HYC processes for the cracking of vacuum-gas-oils into light products such as LPG, naphtha and middle distillates, metal-supported USY zeolite catalysts are widely used [15]. According to the previous study on tetralin HYC, however, metal-supported USY zeolite catalysts showed a limited selectivity to benzene and alkyl-benzenes but high selectivity to compounds heavier than BTX [11,16]. Hence, it is also important to design HYC catalysts with zeolites which can lead to high selectivity of light alkyl-benzenes in the rage of C_6–C_8. For the HYC of tetralin into BTX, metal-supported H-Beta was claimed to give high yield of BTX [11], which requires more systematic studies on the effects of HYD activity of metal, metal/acid balance and acidity of H-Beta on BTX yield. In our recent report [5], Ni/H-Beta catalyst showed a high activity in tetralin HYC for this purpose. However, it was suggested that both its metallic function and acidity have to be further controlled to obtain a high per pass yield of BTX approaching the theoretical yield that can be achieved from tetralin HYC [5].

Herein, we report a systematic study on tetralin HYC over various bifunctional HYC catalysts in order to get further insights of fundamental catalytic behavior. Hence, we investigated the following aspects for tetralin HYC reaction: (1) the effect of metal/acid balance in Ni/H-Beta catalysts having various Ni contents (1, 2, 5 and 10 wt%), (2) use of other metals such as Ni-Sn bimetals or CoMo-S to study the effect of HYD activity of metals in HYC catalysts, (3) the effect of H_2/feed molar ratio, and (4) the effect of zeolite acidity by employing H-Beta having different acidity (SiO_2/Al_2O_3 ratio = 38.0 or 75.0) as the zeolites of HYC catalysts.

2. Experimental

2.1. Preparation of catalysts

Ni/H-Beta catalysts with various Ni contents (1, 2, 5 and 10 wt%) were prepared by wet-impregnation of aqueous solution of nickel(II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) on H-Beta (SiO_2/Al_2O_3 = 38.0 or 75.0, Zeolyst). After aging at room temperature (RT) in air, the Ni-impregnated catalysts were dried at 80 °C in air overnight, and then calcined at 500 °C for 2 h in air. Ni-Sn/H-Beta catalysts were prepared by a sequential wet-impregnation method. Tin precursor solution, which was prepared by dissolving tin chloride dihydrate ($SnCl_2{\cdot}2H_2O$) in 1 M HCl solution, was first impregnated on H-Beta followed by drying at 110 °C for 4 h in air. Then, an aqueous solution of nickel(II) nitrate hexahydrate was impregnated on the Sn-impregnated catalyst. After aging at RT in air, the catalysts were dried at 80 °C in air overnight followed by calcination at 400 °C for 4 h in air. In this way, we prepared various Ni-Sn/H-Beta catalysts such as Ni(2)-Sn(3)/H-Beta, Ni(5)-Sn(3)/H-Beta and Ni(5)-Sn(5)/H-Beta. We also prepared Co(3)-Mo(8)/H-Beta catalyst by a wet-impregnation method with metal precursors of cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$). After impregnation, the catalyst was dried at 80 °C in air overnight followed by calcination at 500 °C for 3 h in air to obtain CoMo(oxides)/H-Beta catalyst. The numbers in the parenthesis denote the weight% of metal on the catalysts.

As a control test, we conducted the HYD of tetralin over the catalysts of Ni, Ni-Sn and CoMo supported on γ-Al_2O_3 (Alfa Aesar, BET surface area = 255 m^2/g, total pore volume = 1.14 cc/g). For this purpose, we prepared Ni(5)/γ-Al_2O_3, Ni(5)-Sn(3)/γ-Al_2O_3 and Co(3)-Mo(8)/γ-Al_2O_3 catalysts by using the same procedure for the preparation of corresponding HYC catalysts described above.

2.2. Catalyst characterizations

We characterized catalysts by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) equipped with Energy Dispersive X-ray Detector (EDX), temperature programmed desorption (TPD) of ammonia (NH_3-TPD), temperature programmed reduction (TPR) and hydrogen pulse chemisorption. X-ray powder diffraction patterns of catalysts were obtained using a Rigaku Miniflex 600 with a Cu Kα X-ray source of wavelength 1.54 Å. TEM images were obtained using a JEM-2010 (JEOL, Japan). H_2 pulse chemisorptions were employed to measure the H_2 uptakes of Ni and Ni-Sn supported catalysts at 308 K using a BEL-CAT instrument (BEL Japan, Inc.) equipped with a thermal conductivity detector. For this purpose, catalysts (0.1–0.14 g) were reduced in H_2 flow at the specific condition given in the catalytic activity test section and then purged in He flow at the reduction temperature for 30 min. After cooling to 308 K, H_2 pulse chemisorptions were started.

2.3. Catalytic activity tests

2.3.1. HYC of tetralin

The HYC reaction test was conducted in a fixed-bed down-flow micro-reactor heated by an electrical furnace under the total pressure of 4 MPa. The reactor pressure was controlled by means of a back pressure regulator and the flow rate of H_2 was controlled by using a mass flow controller. Catalysts were pelletized and sieved into 250–500 μm fractions. In HYC reaction, the sieved catalyst (typically 0.58 g) was loaded in a stainless steel reactor (3/8″ O.D.). Glass beads (1–1.25 mm) were filled in the upper space of catalyst bed so that feed stream is pre-heated and well-distributed down the reactor before entering the catalyst bed. Then, Ni/H-Beta and Ni-Sn/H-Beta catalysts were dried at 450 °C for 2 h in He flow. After cooling down to RT, catalysts were reduced at 450 °C (ramping rate of 5 °C/min) for 1 h in H_2 flow (60 cc/min). After reduction, the reactor temperature was cooled to 120 °C, and reaction feed mixture was introduced into the reactor. The reactor pressure was raised to 4 MPa followed by the reactor temperature increase to a desired temperature. Tetralin feed was introduced to the reactor using an HPLC pump at WHSV = 2.0 h^{-1} and the reaction test was conducted