Applied Catalysis A: General 492 (2015) 140–150

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Selective hydroconversion of naphthalenes into light alkyl-aromatic hydrocarbons

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ARTICLE INFO

Article history:
Received 30 August 2014
Received in revised form 5 November 2014
Accepted 1 December 2014
Available online 23 December 2014

Keywords:
Naphthalenes hydrogenation
Tetralin hydrocracking
BTX
Mo_2C catalyst
Ni/H-Beta

ABSTRACT

2-Ring aromatics such as naphthalene and alkyl-naphthalenes constitute a high fraction in the diesel boiling point range by-products from oil refining and petrochemical plants. A two-step catalytic process, consisting of a selective hydrogenation of naphthalenes to tetralins and a subsequent hydrocracking of tetralins into light alkyl-aromatic hydrocarbons rich in BTX (benzene, toluene, xylenes), was postulated and studied in a fixed bed down-flow reactor under a moderate pressure of 3–4 MPa. For the selective hydrogenation of naphthalenes to tetralins, it was found that the catalytic performances of Mo_2C-supported catalysts were superior in terms of tetralins yield as well as selectivity to the conventional metal-supported catalysts such as Pt, Co, Ni and NiW supported catalysts. The hydrocracking of tetralin was demonstrated to produce light alkyl-aromatic hydrocarbons rich in BTX over a monofunctional H-Beta and a bifunctional Ni/H-Beta catalyst. For the high per pass yield of BTX in the hydrocracking of tetralin in which chemical equilibrium limits its conversion and product selectivity, the bifunctional Ni/H-Beta catalyst was found to be highly promising compared with the monofunctional H-Beta catalyst. The bifunctional Ni/H-Beta showed the BTX selectivity in liquid product and the total BTX yield as high as 69.5% and 40.7 wt%, respectively, at the tetralin conversion of 99.5% at 450 °C under 4 MPa. The catalytic behavior of Ni/H-Beta suggests that BTX yield can be much improved by properly controlling the hydrogenation power of metallic sites (i.e., suppressing the hydrogenation activity), the acidity of H-Beta and their balance on the bifunctional hydrocracking catalysts.

1. Introduction

In oil refining and petrochemical industries, chemically refractory heavy fractions are produced in large quantities as process by-products. Representative examples in diesel boiling point range are the aromatic-rich streams such as light cycle oil (LCO) from fluidized catalytic cracker (FCC) [1,2], and C_{10}^{+} heavy aromatics from naphtha cracking centers (NCC) [3] and para-xylene plants. The major refractory components included in these by-products are naphthalene and alkyl-naphthalenes. Due to the high aromatic hydrocarbon content, they cannot be blended in diesel pools [2] but rather are usually disposed as low-value products such as (1) a blending stock in heavy fuel oil for viscosity adjustment for LCO [1,4] or (2) self-use in plant fuel or heating oil, etc. for C_{10}^{+} heavy aromatics [3]. Since the market demand of heavy fuel oil is in its steady reduction worldwide [5], it is highly desirable to convert these fractions into high-value products, i.e., diesel fuel of high cetane value with low aromatic and sulfur contents [2] or light alkyl aromatic hydrocarbons such as BTX (benzene, toluene and xylenes) [6], of which demands are steadily increasing.

There has been tremendous efforts to develop a two-stage hydrodearomatization of these aromatic-rich fractions to decrease the total aromatic content to less than 10 wt% along with the sulfur content less than 10 ppm for use in diesel [7–9]. However, much less attention has been devoted to the production of BTX from these fractions. Currently, the main source of BTX includes reformate from catalytic reforming, pyrolysis gasoline from NCC and coke oven light oil from coke oven plants. If catalytic solutions to convert these aromatic-rich fractions into high-value BTX were available, they could serve as a supplementary source of BTX or a new “on-purpose” or “stand-alone” process for BTX production. Simply, the overall process economics could be improved considering (1) the historically high price-spread between BTX and heating oil, or (2) the replacement of high price naphtha feedstock for the catalytic reformer with low cost aromatic-rich fractions. Recently, such processes have been reported and patented [6,10,11]. For example,

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http://dx.doi.org/10.1016/j.apcata.2014.12.001
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UOP LLC commercialized the LCO-X process in which catalytic processes such as the hydrotreatment of LCO to reduce contaminants, the conversion of hydrotreated LCO and the aromatic maximization unit are incorporated in series [6].

To achieve high per pass yield of BTX from aromatic-rich fractions, it is important to convert the 2- and 3-ring aromatics into single-ring products in high selectivity. In this regard, we postulated the following two-stage catalytic process (outlined in Scheme 1) to convert naphthalene (for example) into high-value BTX. In the scheme, one ring of naphthalene is selectively hydrogenated into tetralin in the first stage (1) and the naphthenic ring of tetralin is cracked in the second stage (2) to yield BTX and cracking products. By removing polynuclear aromatics in the first stage, the two-stage process would better guarantee the catalyst stability in the second stage since they are highly susceptible to coke formation on the acid sites of subsequent hydrocracking catalyst. In Scheme 1, the final BTX yield will be primarily determined by the hydrogenation selectivity, i.e., naphthalene hydrogenation to tetralin versus to decalins, since the complete hydrogenation of naphthalene to decalins in step (1) will lead to mostly hydrocracked products (LPG and naphtha) instead of high-value BTX along with extensive hydrogen consumption in the hydrocracking step (2).

Fundamental studies concerning the kinetic, mechanistic, thermodynamic and catalytic chemistry aspects of aromatic hydrogenation over conventional hydrogenation catalysts including noble metals and sulfide catalysts were well documented in the literature [8,12]. There are chemical equilibrium limitations on aromatic hydrogenation within the normal operating range of hydrofining over conventional Co-Mo and Ni-Mo sulfide catalysts which become active only at relatively high temperature [8,13,14]. Noble metals including Pt, Pd and Rh are well known active hydrogenation catalysts but are costly and have relatively low resistance to sulfur poisoning. Furthermore, noble metal catalysts used in naphthalene hydrogenation are not selective to tetralin but give high selectivity to decalins at high naphthalene conversion levels [15–19] due to their high catalytic hydrogenation activity. Thus, it is desirable to look for low-cost, contaminant-tolerable and active aromatics hydrogenation catalysts that have high selectivity to tetralin in the first stage of Scheme 1 above. For this purpose, molybdenum carbide (Mo_2C) is of interest due not only to its similar catalytic activity to noble metals [20–23] but its high tolerance to sulfur [24–27] and high hydrotreating (HDT) capability of gas oils similar to the commercial HDT catalysts such as NiMo-S and CoMo-S catalysts [25,26]. Recently, Pang et al. [28] prepared Mo_2C/AC (Mo_2C supported on activated carbon) by a microwave-assisted pyrolysis method and showed that the Mo_2C/AC has a moderate hydrogenating capability to give high selectivity to tetralin in the hydrogenation of naphthalene. Mo_2C-supported HY catalytic systems were intensively studied as a replacement for noble metal loaded catalysts, aimed at the conversion of naphthalene into high-cetane diesel components via the hydrogenation and ring opening of naphthalene [27,29–31]. Others have studied the direct hydroconversion of methyl-naphthalene to alkyl-benzenes [4,32] or the hydrocracking of tetralin [33–36] as the probe reaction for the purpose of heavy-oil upgrading to high quality diesel fuel rather than to high-value BTX. The product distribution from hydrocracking is strongly dependent upon zeolites employed in the hydrocracking catalysts at fixed metallic functions. Some previous reports on the hydrocracking of 1-methyl naphthalene [4,32] and tetralin [33] on metal-supported USY zeolite catalysts revealed that the BTX selectivity in the product was not high enough for the purpose of high value BTX production.

In the present work, Mo_2C-supported catalysts, $Mo_2C/\gamma\text{-}Al_2O_3$ and Mo_2C/Na-Y, were prepared and tested in the hydrogenation of naphthalene and methyl-naphthalene under a moderate H_2 pressure of 3 MPa. Their catalytic activity and the resulting product selectivity to tetralin over decalins were compared with those from the conventional metal-supported catalysts, $Ni/\gamma\text{-}Al_2O_3$, $Co/\gamma\text{-}Al_2O_3$, $Pt/\gamma\text{-}Al_2O_3$ and $NiW/\gamma\text{-}Al_2O_3$. Finally, the hydrocracking of tetralin was studied over a monofunctional H-Beta and a bifunctional Ni/H-Beta catalyst to demonstrate the two-stage catalytic process (Scheme 1) for the production of BTX from heavy-aromatics rich in naphthalenes.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Hydrogenation (HYD) catalysts

The catalysts for the HYD of naphthalenes, $Mo_2C(x)/\gamma\text{-}Al_2O_3$ with $x = 5$, 10 and 20, $Mo_2C(20)$/Na-Y, $Ni(5)/\gamma\text{-}Al_2O_3$, $Co(5)/\gamma\text{-}Al_2O_3$, $Pt(1)/\gamma\text{-}Al_2O_3$ and NiW (NiO = 3.5 wt%; WO_3 = 24.0 wt%)/$\gamma\text{-}Al_2O_3$ catalysts were prepared, where the numbers in the parenthesis denote the weight % of metal on the catalysts. The Mo_2C-supported catalysts were prepared by temperature-programmed reaction of molybdenum oxides in CH_4 (20%)/H_2 flow following the procedure in the literature [30]. $\gamma\text{-}Al_2O_3$ (Alfa Aesar) and Na-Y (CBV100, Zeolyst) were employed as the supports of HYD catalysts.

The ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) aqueous solution containing the required amount of Mo, was impregnated on the supports. After aging at room temperature for 1 h, the Mo impregnated catalysts were dried at 80 °C in air overnight followed by calcination at 500 °C for 4 h under O_2 flow. The calcined catalysts were placed in a quartz reactor with frit and heated to 700 °C at a rate of 5 °C/min in a CH_4/H_2 flow (20% CH_4) and held at 700 °C for 4 h. The catalysts were then held for 2 h in a H_2 stream to remove excess carbon before cooling down to room temperature. Finally, the catalysts were passivated in an O_2 (1%)/He flow for 45 min and stored in a globe box filled with Ar.

The $Ni(5)/\gamma\text{-}Al_2O_3$, $Co(5)/\gamma\text{-}Al_2O_3$, $Pt(1)/\gamma\text{-}Al_2O_3$ and $NiW/\gamma\text{-}Al_2O_3$ catalysts were also prepared by a wet-impregnation method with the metal precursors, nickel(II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$), ammonium metatungstate hydrate ($(NH_4)_6(H_2W_{12}O_{40})\cdot 5H_2O$) and hexachloroplatinic acid (H_2PtCl_6), respectively. After aging at room temperature for 1 h, the metal-impregnated catalysts were dried at 80 °C in air overnight. The $Ni/\gamma\text{-}Al_2O_3$, $Co/\gamma\text{-}Al_2O_3$ and $NiW/\gamma\text{-}Al_2O_3$ catalysts were calcined at 500 °C in air for 2–3 h while the $Pt/\gamma\text{-}Al_2O_3$ catalyst was calcined at 350 °C in an O_2 flow for 4 h.

2.1.2. Hydrocracking (HYC) catalysts

The catalyst for the HYC of tetralin, Ni(2)/H-Beta, was prepared by wet-impregnation of aqueous solution of nickel(II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$) on H-Beta (CP811E-75, SiO_2/Al_2O_3 = 75, Zeolyst) using the same procedure for the preparation of $Ni/\gamma\text{-}Al_2O_3$ catalyst. The Ni loading amount was 2 wt%. H-Beta (CP811E-75, SiO_2/Al_2O_3 = 75, Zeolyst) was also employed as a monofunctional HYC catalyst for reference.

2.2. Characterization of the catalysts

The catalysts were characterized by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), temperature programmed reduction (TPR) and pulse chemisorption of CO or H_2. X-ray powder diffraction patterns were obtained using a Rigaku Miniflex 600 with a Cu Kα X-ray source of wavelength 1.54 Å. Measurement was performed using a scan range 5–80° with a step width of 0.02° and scan speed of 0.2°/min. XPS analysis was done using a Theta Probe AR-XPS System (Thermo Fisher Scientific, UK) with a monochromated Al Kα