Applied Catalysis B: Environmental 219 (2017) 1–9

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Rational synthesis of silylated Beta zeolites and selective ring opening of 1-methylnaphthalene over the NiW-supported catalysts

Su-Un Lee, You-Jin Lee, Jeong-Rang Kim*, Soon-Yong Jeong

Carbon Resources Institute, Korea Research Institute of Chemical Technology, 141, Gajeong-ro, Yuseong-gu, Daejeon 34114, South Korea

ARTICLE INFO

Article history:
Received 25 April 2017
Received in revised form 10 July 2017
Accepted 17 July 2017

Keywords:
Bi-functional catalyst
Beta zeolite
Silylation
Selective ring opening
1-methylnaphthalene

ABSTRACT

Heavy oil has been by-produced from refinery and petrochemical processes, and its use as low-value fuels has been restricted by stricter environmental regulations due to heavy molecules, multi-ring aromatics, and high sulfur content. In a bi-functional catalyst system of metal and zeolitic acid, balancing metallic (from metal element) and acidic function (from zeolite elements) is essential for harnessing the selective ring opening (SRO) reaction with the aim of upgrading the heavy oil. Here, we report a synthetic strategy to control the acid site distribution of Beta zeolite through the silylation reaction with tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS), and tetrabutyl orthosilicate (TBOS) as silylation agents. As the size of alkyl chain group in the silylation agents gets larger, the silylation agents were suppressed to spread into the channels and thus the formation of SiO_2 layer was intentionally occurred on the external surface of the zeolite. Resulting from the selectively deposited SiO_2 layer, NiW metals supported on each silylated Beta zeolite altered the metal distribution and further the balance of metallic and acidic function. NiW catalyst supported on TBOS-silylated Beta zeolite exhibited the best catalytic performance toward the SRO reaction of 1-methylnaphthalene in a fix-bed reaction system, proving the optimal balance of metallic and acidic functions. We expect that this study will benefit the control over the selective silylation reaction in order to optimize the balance of metallic and acidic functions in the bi-functional catalysts, and, hence, to promote properly aromatic saturation (hydrogenation) and ring opening (hydrocracking) for selective ring opening products.

1. Introduction

Zeolites are crystalline aluminosilicates of various structures containing large active surfaces and ordered micropore network, which accommodate a wide range of industrial applications such as gas adsorption, ion exchange, and separation [1,2]. Especially, the basic structural unit of zeolite frameworks consists of silicon or aluminium atoms tetrahedrally coordinated to four oxygen atoms, but replacing Si^{4+} by Al^{3+} crates a negative charge on the framework [3]. When zeolite framework charges are neutralized by protons, they create acid sites that can facilitate acid-catalyzed reactions, such as isomerization, alkylation, and cracking for hydrocarbons [4,5].

Heavy oil has been by-produced from refinery and petrochemical processes and used as low grade fuel. However, its use has been restricted by stricter environmental regulations due to heavy molecules, multi-ring aromatics, and high sulfur content in the heavy oil. Due to the regulations and persistent high oil prices, upgrading process of heavy oil to high-value middle distillates with low aromatics has attracted interest to many researchers. In the requirements of improving environmental protection and the low-value heavy oil, the acid sites of zeolites have been widely applied for converting the heavy oil to high-value lighter products [6]. More interestingly, multi-ring aromatics, the major components of the heavy oil, can be converted through the selective aromatics ring opening (SRO) reaction into lighter aromatics including benzene, toluene, ethyl-benzene, and xylene (BTEX) [7]. However, for high yield toward desirable mono-ring aromatics, aromatic saturation (hydrogenation) and ring opening (hydrocracking) should be properly proceeded to maintain mono-ring aromatics and avoid the loss into excessive cracked fractions [7,8].

By introducing metal elements into zeolites, not only acidic function from zeolites but also metallic function from metal elements can promote ring opening and aromatic saturation step, respectively, as bi-functional catalytic system [8–10]. To fully exploit the advantages of bi-functional catalytic system, balancing the functions of metal and zeolites is critical in the way of controlling the ratio of metal to acid sites [11–13] and the proximity between both sites [14–17]. In particular, the acid sites on zeolites

---

* Corresponding author.
E-mail address: jrkim@krict.re.kr (J.-R. Kim).

http://dx.doi.org/10.1016/j.apcatb.2017.07.047

can influence the catalytic conversion and selectivity depending on being located on the external surface or channels [2,3]. Furthermore, the different metal-support interaction induced by being deposited on these acid sites can alter the electronic properties of metal [18]. Taken together, once the correlation of the catalytic activities according to the distribution of the acid sites and their metal-zeolite interaction is clarified, it will pave an alternative way to give fine control over the bi-functional catalyst system. However, due to the complexity of maneuvering the acid site distribution of the zeolite, the realization of such bi-functional catalysts has been rarely reported.

Generally, common post-synthetic methods to control the acid sites are cation exchange and dealumination [19]. Cation exchange decreases Brønsted acidity and leaves Lewis acid sites intact. Alternatively, dealumination (i.e., in HCl) removes framework Al cations and leaves behind SiOH as vacancies, decreasing Lewis and Brønsted sites. Although both post-synthetic methods are well established, selectively tuning the distribution of the acid sites has been limited. One feasible method is the formation of mild Brønsted sites via silylation reaction onto hydroxyl groups on the surface of zeolite, which form Si—O—Si or Si—O—Al bonds to lose sufficient strength to crack as the original acid sites [20]. With adopting the silylation agents in larger molecular size than the pore opening of the zeolites, the silylation agents are hindered to diffuse into the pores, so the deposition of SiO_2 layer can be intentionally conducted on the external surface [21]. In this respect, the silylation reaction can enable to investigate the function of acid sites in channels, apart from in the external surface.

Herein, we report a novel synthetic strategy to modify the distribution of acid sites on the external surface and channels in zeolites. As for a bi-functional catalysts targeting the SRO reaction, Beta zeolite with SiO_2/Al_2O_3 molar ratio of 38 (denoted as Beta(38)) was chosen because of the sufficient pore opening of 5.7 × 7.5 Å to diffuse the bulky of multi-aromatics [22]. Based on the silylation reaction, the distribution of the acid sites on the zeolites was modified by varying the alkyl chain of the silylation agents as tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS) and tetrabutyl orthosilicate (TBOS). The silylation agents with the different alkyl chain were employed due to our expectation that the SiO_2 layer can be selectively overcoated to the external surface or channels in accordance with the molecular size of their silylation agents. To investigate the relationship with the distribution of acid sites and catalytic performance of the bi-functional catalysts, NiW catalysts supported on three types of silylated Beta(38) were applied for the SRO reaction of 1-methyl naphthalene (1-mNap) as a model reaction of multi-ring aromatics. The present study can give a rational guideline for the modification of zeolite acid sites with proper silylation agents, and will contribute to devise the efficient bi-functional catalysts.

2. Experimental section

2.1. Catalyst preparation

2.1.1. Silylated-Beta(38)

Silylated-Beta(38) zeolite materials were prepared by following the literature with some modifications [20]. Commercial Beta zeolite (CP814C, SiO_2/Al_2O_3 mole ratio = 38) purchased from Zeolyst Co. was calcined in air atmosphere at 550 °C for 5 h in order to remove impurities and obtain the hydrogen-form zeolite from the ammonium-form. The zeolite (2 g) was mixed with a 50.0 ml of hexane in a three-neck equipped with a reflux condense, and then the solution was heated to 70 °C under moderate stirring. When the solution was maintained at 70 °C, silylation agents corresponding to a loading of 4.0 wt% SiO_2 was injected into the mixture. Depending on the alky chain of the silylation agents, 0.2 ml of tetramethyl orthosilicate (TMOS), 0.3 ml of tetraethyl orthosilicate (TEOS) or 0.489 ml of tetrabuthyl orthosilicate (TBOS) was added, respectively. After the mixture was kept for1 h, hexane was removed from the resulting solution by aspiration. The samples were dried at 120 °C for 12 h and calcined in air atmosphere at 500 °C for 4 h. Three types of silylated Beta(38) zeolite were denoted as TMOS-, TEOS-, and TBOS-silylated Beta(38), and compared with Beta(38) zeolite untreated by the silylation.

2.1.2. NiW/silylated-Beta(38) and NiW/Beta(38)

As bi-functional catalysts, NiW/silylated-Beta(38) and NiW/Beta(38) were prepared by a co-impregnation method with an aqueous solution of the appropriate amounts of nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, 98%, purchased from Samchun) and ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$, 66.5 wt%, purchased from Sigma-Aldrich). The 1.1 mmol of Ni and 1.1 mmol of W per 1 g of zeolite were loaded onto as-prepared Beta(38), TMOS-silylated Beta(38), TEOS-silylated Beta(38) and TBOS-silylated Beta(38), respectively. After the impregnation step, the water solvent was removed under vacuum in a rotary evaporator. The collected powder sample was dried at 120 °C in an oven for 12 h, and followed by calcination in an air atmosphere at 550 °C for 4 h.

2.1.3. NiW/Silica(Q-3)

Commercial amorphous silica (Q-3, average pore diameter = 3 nm) purchased from Fusi silysia chemical LTD. was calcined in air atmosphere at 550 °C for 5 h in order to remove impurities. NiW/Silica(Q-3) was prepared as the same procedure for NiW/Beta(38) and NiW/silylated Beta(38). The 1.1 mmol of Ni and 1.1 mmol of W per 1 g of silica (Q-3) were loaded onto as-prepared Silica(Q-3), and then the water solvent was removed under vacuum in a rotary evaporator. The collected powder sample was dried at 120 °C in an oven for 12 h, and followed by calcination in an air atmosphere at 550 °C for 4 h.

2.2. Catalyst characterization

Wide angle powder X-ray diffraction (XRD) patterns were obtained with a Rigaku Ultima IV Diffractometer (40 kV, 40 mA, Cu-Kα radiation) in the 2θ range of 5–80° using a PDXL program. Transmission electron microscopy (TEM) images and TEM-energy-dispersive X-ray spectroscopy (TEM-EDS) elemental analysis were taken using a field emission gun transmission and scanning transmission electron microscope (FEG-S/TEM, FEI-Talos F200S) operating at 200 kV. The bulk elemental composition was determined by inductively-coupled plasma-atomic emission spectrometer (ICP-AES, SHIMADZU ICPS-1000IV) after the dissolution of the sample in the mixture of HF and H_2NO_3, in which the enrichment of Si was observed in consideration of conventional Beta(38) zeolite known as Si/Al = 19. To measure N_2 adsorption/desorption isotherms, the sample was degassed under vacuum at 200 °C for 6 h and N_2 adsorption/desorption was carried out at −196 °C by using a Micromeritics ASAP2020 instrument. The total surface area was calculated by the BET equation, and the pore volume was measured from the total N_2 adsorption amount. The temperature programming desorption of ammonia (NH_3-TPD) was carried out for acidity measurement using BELCAT-B equipped with a thermal conductivity detector (TCD). The sample was pretreated in a H_2 (5%)/Ar flow at 400 °C for 100 min, then cooled down to 100 °C under a He flow. The sample was exposed to a NH_3 (30 mol%)/He flow for 30 min, followed by purging in the He flow for 90 min for elimination of weakly physisorbed ammonia. The sample was heated in the He flow from 100 °C to 500 °C at a heating rate of 10 °C/min and the amount of the desorbed ammonia was detected by TCD.