Article

Journal of
Nanoscience and Nanotechnology
Vol. 16, 1715–1719, 2016
www.aspbs.com/jnn

Selective Ring Opening of 1-Methylnaphthalene Over NiW-Supported Catalyst Using Dealuminated Beta Zeolite

Eun-Sang Kim[1,2], You-Jin Lee[1,2], Jeong-Rang Kim[1,*], Joo-Wan Kim[1], Tae-Wan Kim[1], Ho-Jeong Chae[1], Chul-Ung Kim[1], Chang-Ha Lee[2], and Soon-Yong Jeong[1]

[1] *Research Center for Green Catalysis, Korea Research Institute of Chemical Technology, Daejeon 305-600, South Korea*
[2] *Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 102-749, South Korea*

Nanoporous Beta zeolite was dealuminated by weak acid treatment for reducing the acidity. Bi-functional catalysts were prepared using commercial Beta zeolites and the dealuminated zeolites for acidic function, NiW for metallic function. 1-Methylnaphthalene was selected as a model compound for multi-ring aromatics in heavy oil, and its selective ring opening reaction has been investigated using the prepared bi-functional catalysts with different acidity in fixed bed reaction system. The dealuminated Beta zeolites, which crystal structure and nanoporosity were maintained, showed the higher SiO_2/Al_2O_3 ratio and smaller acidity than their original zeolite. NiW-supported catalyst using the dealuminated Beta zeolite with SiO_2/Al_2O_3 mole ratio of 55 showed the highest performance for the selective ring opening. The acidity of catalyst seemed to play an important role as active sites for the selective ring opening of 1-methylnaphthalene but there should be some optimum catalyst acidity for the reaction. The acidity of Beta zeolite could be controlled by the acid treatment and the catalyst with the optimum acidity for the selective ring opening could be prepared.

Keywords: Selective Ring Opening, 1-Methylnaphthalene, BTEX, Beta Zeolite, Dealumination, Acidity.

1. INTRODUCTION

Heavy oil, by-produced from petrochemical industries and oil refinery, has been used as cheap fuel. The heavy oil contains many heavy molecules, multi-ring aromatics, and asphaltenes with high sulfur content. Rigorous environmental regulations have restricted the use of the heavy oil as the fuel. Due to the regulations and persistent high oil prices, upgrading process of heavy oil to high-value middle distillates with low aromatics have attracted interest to many researchers.[1]

Multi-ring aromatics, especially naphthenic molecules such as naphthalene and methyl-naphthalenes, are the major components of heavy oil. Partial aromatic saturation of the naphthenic molecule can form tetralinic molecule, and alkyl-benzenes including benzene, toluene, ethyl-benzene, and xylene (BTEX) can be produced by following cracking of the naphthenic ring of the tetralinic molecule.[2] In other words, selective ring opening (SRO) should be a potential route for the production of valuable compounds from heavy oil.[3]

Bi-functional catalytic system (metallic and acidic functions) is required in the SRO of naphthenic molecules.[2,4] A metallic function is required for hydrogenation step (aromatic saturation) and an acidic function for the ring opening step.[5,6] The balance between the metallic function and the acidic function is necessary. Several studies have been carried out for the production of mono aromatic compounds, such as BTEX, by the SRO of naphthenic molecules. Kim et al. carried out the SRO of naphthalene for BTEX using Ni_2P/zeolites (SiO_2, ZSM-5, Beta, USY) as catalyst and reported that Ni_2P/Beta catalyst showed the high performance.[7]

In this study, nanoporous Beta zeolite was dealuminated by acid treatment for reducing the acidity. Bi-functional catalysts were prepared using Beta zeolites and the dealuminated Beta zeolites for acidic function, NiW for metallic function. 1-Methylnaphthalene (1mNap) was selected as a model compound for multi-ring aromatics in heavy oil, and its SRO has been investigated using the prepared bi-functional catalysts with different acidity in fixed bed reactor system.

---

[*] Author to whom correspondence should be addressed.

1533-4880/2016/16/1715/005 doi:10.1166/jnn.2016.11997

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

The dealuminated Beta zeolites were synthesized by acid treatment with oxalic acid.[8] Beta zeolite ($SiO_2/AlO_3 = 38$, CP814C) purchased from Zeolyst Co. was calcined in air atmosphere at 550 °C for 6 h in order to remove impurities and obtain the hydrogen-form zeolite from the ammonium-form. The zeolite (2 g) was added to the aqueous oxalic acid solution (100 cm^3) with pH 2 and the sus-pension was stirred at 60 °C for 4 h or 8 h, filtered, and washed with hot water to remove aluminum complexes formed. The dealuminated zeolites were dried in an oven at 120 °C for 12 h. The SiO_2/AlO_3 mole ratio of the dealuminated zeolites was determined by ICP-AES. The ratio of the zeolite dealuminated for 4 h was 55, and 80 for 8 h.

The bi-functional catalysts including NiW were prepared by wet impregnation method using two commercial Beta zeolites of Zeolyst Co. (CP814E, CP814C) and the two dealuminated Beta zeolites, which SiO_2/Al_2O_3 mole ratios were 25, 38, 55, and 80. Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40} \cdot H_2O$) were used as the precursor for each metal. Before reaction test, the catalyst was sulfidated in $H_2S(10\%)/H_2$ flow at 350 °C for 3 h using a tubular furnace. The impregnation amount of Ni was 1.1 mmol/g-zeolite and the amount of W was the same. The prepared catalysts were denoted as "NiW/Beta(a)," where 'a' is a SiO_2/Al_2O_3 mole ratio of Beta zeolite.

2.2. Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Multiplex (40 kV, 1.6 kW, Cu-Kα radiation). Surface area and pore volume were measured by N_2 adsorption using a Micromeritics ASAP2020 instrument. Transmission electron micrographs (TEM) were taken on a Philips Tecnai G220 device operated at 200 kV. Scanning transmission electron microscopy (STEM)/energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were taken with a Tecnai G2 F30 instrument with an accelerating voltage of 300 kV. Temperature-programmed desorption of ammonia (NH_3-TPD) was carried out for the total acidity of prepared samples using a BELCAT-B instrument.

2.3. Catalytic Performance Tests

The performances of prepared catalysts for the SRO of 1mNap were measured at 400 °C and 50 barg using a fixed-bed reaction system. The sulfidated catalyst (1 g) was loaded in the reactor, followed by leak test. The catalyst was pretreated in H_2 flow at 400 °C and atmospheric pressure for 8 h and the pressure increased to 50 barg. The liquid feed of 1mNap was delivered at flow rate of 0.037 cm^3/min using a liquid pump along with H_2 flow of 175 SCCM (H_2/1mNap mol ratio = 30). The reaction product was cooled down to 5 °C and the liquid product was collected every 2 or 3 hours. Gas yield was calculated from the weight of the liquid product. The liquid product was analyzed by gas chromatography coupled with mass spectrometry (GC-MS, Agilent 7890A/5975C) for qualitative analysis and a frame ionization detector (GC-FID, Younglin 6100) for quantitative analysis. Both of them were equipped with DB-5MS UI capillary column.

3. RESULTS AND DISCUSSION

The XRD patterns of the dealuminated Beta zeolites and the prepared NiW/Beta catalyst were shown in Figure 1. The XRD patterns of the dealuminated zeolites, Beta(55) and Beta(80), showed the same patterns as its original zeolite, Beta(38). It meant that the crystal structure of the zeolite was not collapsed but maintained after dealumination. The XRD patterns of NiW/Beta(38) catalyst showed the same patterns as Beta(38) zeolite and none of metal diffraction peaks was observed in the XRD patterns of the catalyst. It might be mainly owing to the nanosized metal particles below the detection limit of this technique and indicate that the metals should be well dispersed as nanoparticles in the zeolite. In case of the catalysts using

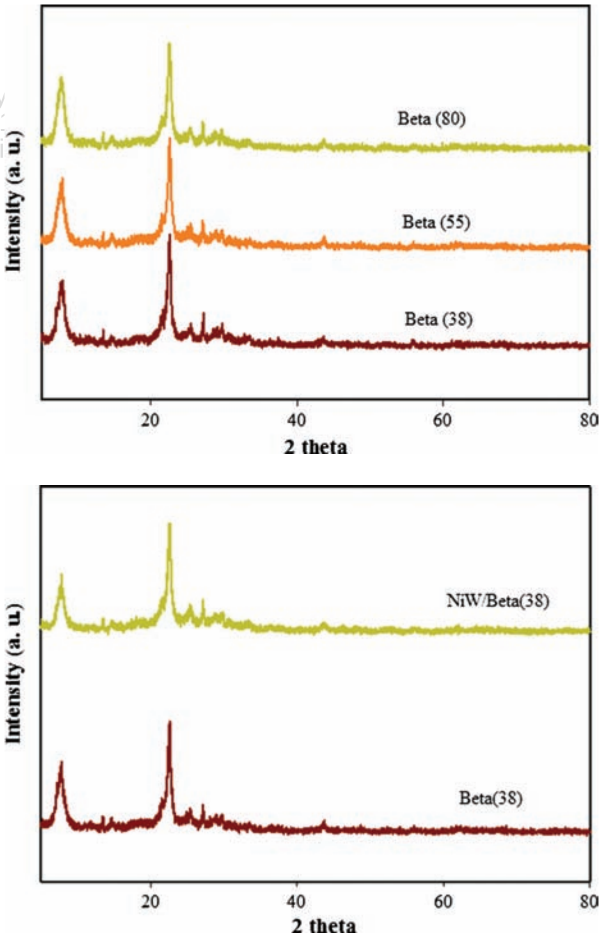

Figure 1. XRD patterns of dealuminated Beta zeolites and NiW/Beta catalyst.

Table I. Physical properties of Beta zeolites and NiW/Beta catalysts.

	Surface area (m^2/g)			Pore volume (cm^3/g)		
Sample	Total	Micropore	Mesopore	Total	Micropore	Mesopore
Beta(25)	558	368	190	0.71	0.17	0.54
Beta(38)	588	465	123	0.32	0.22	0.10
Beta(55)	590	456	134	0.32	0.21	0.11
Beta(80)	588	425	163	0.34	0.20	0.13
NiW/Beta(25)	399	301	98	0.37	0.14	0.23
NiW/Beta(38)	426	342	84	0.22	0.16	0.06
NiW/Beta(55)	384	307	77	0.2	0.14	0.04
NiW/Beta(80)	357	281	76	0.19	0.13	0.06

Beta zeolites with different SiO_2/Al_2O_3 mole ratios, the identical XRD patterns to Figure 1 were observed and the results is not shown in this paper.

Surface area and pore volume of the Beta zeolites and the NiW/Beta catalysts were shown in Table I. The total surface area was calculated by the BET equation. The area and volume of the nanosized pores (micropore and mesopore) were calculated by the *t*-plot method. The dealuminated zeolites, Beta(55) and Beta(80), showed the slightly high mesopore area and low micropore area. Anyway, their nanoporosities were similar to its original zeolite, Beta(38) and the pore structure of the zeolite was also maintained after dealumination. NiW impregnation into Beta zeolites decreased their micropore and mesopore, indicating that the metal species are well distributed as nanoparticles in both the micropore and mesopore of the zeolite.

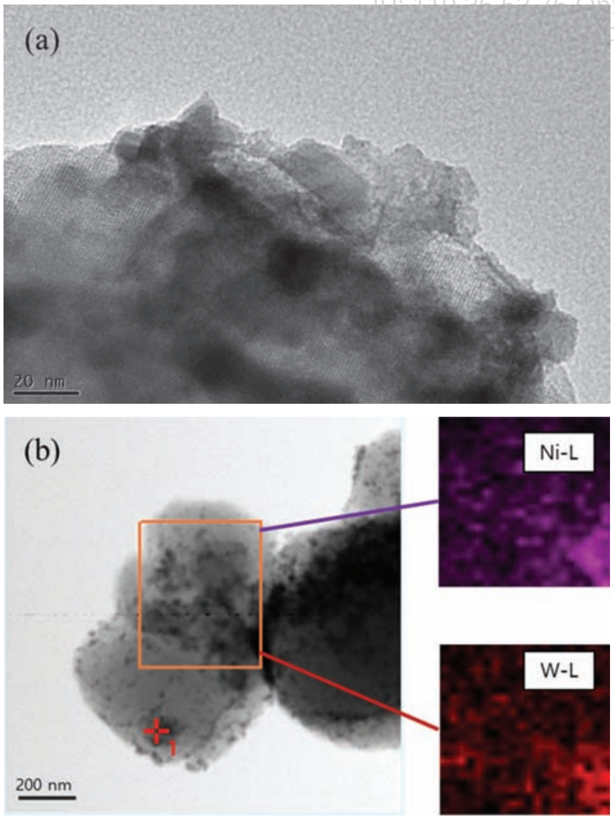

Figure 2. (a) TEM image and (b) STEM/EDS elemental mapping images of NiW/Beta(38) catalyst.

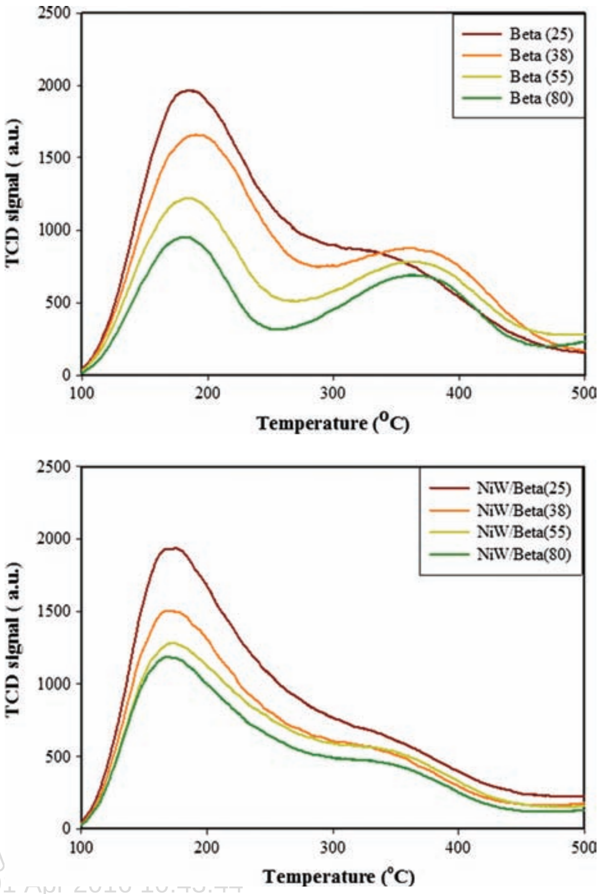

Figure 3. NH_3-TPD profiles of Beta zeolites and NiW/Beta catalysts.

The TEM image and the STEM/EDS elemental mapping images of NiW/Beta(38) catalyst were shown in Figure 2. The characteristic porous structure of the zeolite was observed with no noticeable particles of Ni and W in the TEM image. The interstitial space between the zeolite crystal particles in the agglomeration might act as mesopore. Each metal seemed to be well dispersed in the mesopore as well as the characteristic micropore of the zeolite from the elemental mapping images. In case of the catalysts using Beta zeolites with different SiO_2/Al_2O_3 mole ratios, the similar images to Figure 2 were observed and the results is not shown in this paper.

The NH_3-TPD profiles and total acidity of the Beta zeolites and the NiW/Beta catalysts were displayed in

Table II. Total acidity of Beta zeolites and NiW/Beta catalysts.

Sample	Total acidity (mmol/g)	Sample	Total acidity (mmol/g)
Beta(25)	1.113	NiW/Beta(25)	1.081
Beta(38)	0.911	NiW/Beta(38)	0.842
Beta(55)	0.836	NiW/Beta(55)	0.776
Beta(80)	0.583	NiW/Beta(80)	0.673

Table III. SRO performances of NiW/Beta catalysts: 1mNap conversion and product yield distribution.

		Yield, wt%							
Catalyst	1mNap conv., wt%	Gas	Light HC	Ring opening (BTEX)	Hydrogenation	Nap	2mNap	Alkyl-nap	Heavy HC
NiW/Beta(25)	98.7	45.8	7	**42.7 (33.2)**	<1	<1	1.3	1.6	<1
NiW/Beta(38)	98.2	34.3	7.5	**49.6 (39.5)**	1.6	1.3	3.6	5.2	1.6
NiW/Beta(55)	**99.8**	**39.2**	**5.8**	**54.3 (44.9)**	**<1**	**<1**	**<1**	**<1**	**<1**
NiW/Beta(80)	75.5	24.9	4.4	**23.3 (16.2)**	16.7	<1	7.4	3.1	<1

Figure 3 and Table II. The total acidity was determined by NH_3-TPD profile. According to the NH_3-TPD profiles of Beta zeolites, typical two NH_3 desorption peaks for zeolite were observed around 180 °C (weak acid site) and 370 °C (strong acid site). The dealuminated zeolites, Beta(55) and Beta(80), showed the smaller acidity than its original zeolite, Beta(38), as expected. The larger SiO_2/Al_2O_3 mole ratio of Beta zeolite, the smaller total acidity was observed in the NH_3-TPD results as the well-known. It observed that NiW impregnation into Beta zeolites decreased their acidity, except for Beta(80) zeolite with small acidity. It would be because the metals could block acid sites of zeolite but themselves provide acid sites.[9] Accordingly, the impregnation of the metals could increase the acidity, especially for the zeolites with small acidity. Anyway, the acidity of the NiW/Beta catalysts was also inversely proportional to SiO_2/Al_2O_3 ratio of Beta zeolite.

The SRO performances of NiW/Beta catalysts at reaction time of 10 h were shown in Table III and compared with total acidity of the catalyst, based on SiO_2/Al_2O_3 mole ratio of Beta zeolite, as shown in Figure 4. All catalysts maintained the similar performance for about 12 h of reaction time. Most of gas product consisted of alkanes (carbon number 1~4) and light hydrocarbons was cycloalkanes lighter than BTEX. Ring opening species, the most important for the SRO reaction, consisted of alkyl-benzenes including BTEX. Hydrogenation species included tetralin, decalin, and alkyl-tetralins, and heavy hydrocarbons were multi-ring aromatics heavier than two-ring aromatics. In case of the catalysts using the commercial Beta zeolites, both NiW/Beta(25) and NiW/Beta(38) catalysts maintained the high 1mNap conversion over 98%. NiW/Beta(38) with smaller acidity showed the higher yields of ring opening species and BTEX.

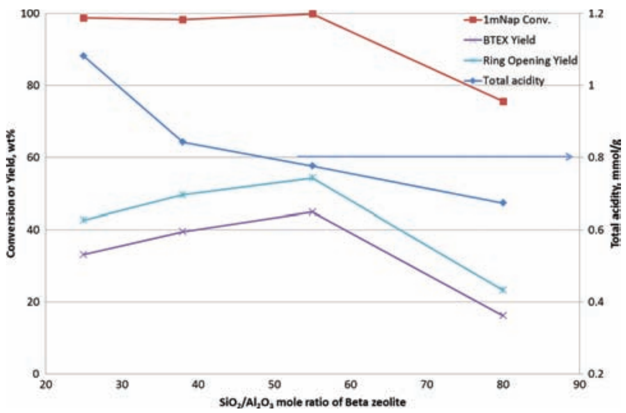

Figure 4. Total acidity and the reaction performances of NiW/Beta catalysts.

In order to prepare the catalyst with higher performance for the SRO reaction, Beta(38) zeolite was dealuminated by weak acid treatment and its acidity was diminished as NH_3-TPD results. The catalyst using the dealuminated Beta zeolite, Beta(55), showed the improved performance for the SRO reaction. However, in case of the catalyst using Beta(80), the 1mNap conversion and yields of ring opening species and BTEX decreased greatly and the yield of hydrogenation species increased, which should be produced by relatively strong metallic function of the catalyst. Therefore, it was confirmed that NiW/Beta(80) catalyst could not provide the sufficient acidic function for the SRO reaction.

The trend between the catalytic performance and its acidity was more obvious in Figure 4. The acidity of NiW/Beta catalysts decreased with SiO_2/Al_2O_3 ratio of Beta zeolite. NiW/Beta(55) catalyst with the moderate acidity showed the highest performance for the SRO reaction, and consequently was believed as the most favorable catalyst for the reaction. The acidity of catalyst seemed to play an important role as active sites for the SRO of 1mNap but there should be some optimum catalyst acidity for the reaction. The acidity of Beta zeolite could be controlled by the weak acid treatment and the catalyst with the optimum acidity for the SRO reaction could be prepared.

4. CONCLUSION

Nanoporous Beta zeolite was dealuminated by weak acid treatment for reducing the acidity. Bi-functional catalysts were prepared using commercial Beta zeolites and the dealuminated zeolites for acidic function, NiW for metallic function. 1mNap was selected as a model compound for multi-ring aromatics in heavy oil, and its SRO reaction has been investigated using the prepared bi-functional catalysts with different acidity in fixed bed reaction system. The dealuminated Beta zeolites, which crystal structure and nanoporosity were maintained, showed the higher SiO_2/Al_2O_3 ratio and smaller acidity than their original zeolite. NiW-supported catalyst using the dealuminated

Beta zeolite with SiO_2/Al_2O_3 mole ratio of 55 showed the highest performance for the SRO reaction. The acidity of catalyst seemed to play an important role as active sites for the SRO of 1mNap but there should be some optimum catalyst acidity for the reaction. The acidity of Beta zeolite could be controlled by the acid treatment and the catalyst with the optimum acidity for the SRO reaction could be prepared.

Acknowledgment: This work was supported by the Korean Institute of Energy Technology Evaluation and Planning (20122010200050).

References and Notes

1. M. S. Rana, V. Samano, and J. Ancheyta, *Fuel* 86, 1216 (**2007**).
2. G. B. McVicker, M. Daage, M. S. Touvelle, C. W. Hudson, D. P. Klein, W. C. Baird, Jr., B. R. Cook, J. G. Chen, S. Hantzer, D. E. W. Vaughan, E. S. Ellis, and O. C. Feeley, *J. Catal.* 210, 137 (**2002**).
3. D. Santi, T. Holl, and V. Calemma, *Appl. Catal. A* 455, 46 (**2013**).
4. V. Calemma, R. Giardino, and M. Ferrari, *Fuel Process. Technol.* 91, 770 (**2010**).
5. K. Sato, Y. Iwata, and Y. Miki, *J. Catal.* 186, 45 (**1999**).
6. K. Sato, Y. Iwata, T. Yoneda, A. Nishijima, Y. Miki, and H. Shimada, *Catal. Today* 45, 367 (**1998**).
7. Y. S. Kim, G. N. Yun, and Y. K. Lee, *Catal. Commun.* 45, 133 (**2014**).
8. R. Srivastava, N. Iwasa, and S. Fujita, *Catal. Lett.* 130, 655 (**2009**).
9. S. J. You, I. G. Baek, and E. D. Park, *Appl. Catal. A* 466, 161 (**2013**).

Received: 14 April 2015. Accepted: 21 April 2015.