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Original Paper

Surface dealuminated Beta zeolites supported WO₃ catalyst and its catalytic performance in tetralin hydrocracking



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ABSTRACT

In this study, selective dealumination of Beta zeolites was performed through partially removing the templating agent in Beta zeolites by calcination and then removing the aluminum on the external surface of Beta zeolites with acid treatment. Hydrocracking catalysts were prepared by loading WO₃ onto these dealuminated Beta zeolites. It was shown that the surface SiO₂/Al₂O₃ of selectively dealuminated Beta zeolites was higher than that of conventionally dealuminated samples for the same bulk SiO₂/Al₂O₃, and the hydrogenation activity of the catalyst of the selectively dealuminated Beta zeolites was lower than that of conventionally dealuminated Beta zeolites for tetralin hydrocracking to BTX showed that the catalysts based on the selectively dealuminated Beta zeolites had higher BTX selectivity and lower coke formation rate than that the catalysts based on the conventionally dealuminated Beta zeolites.

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1. Introduction

Light cycle oil (LCO) obtained from the fluidized catalytic cracking (FCC) process is a low value-added product (Gutiérrez et al., 2011, 2012; Peng et al., 2019; Laredo et al., 2018), which is rich in polycyclic aromatic hydrocarbons (bicyclic and tricyclic hydrocarbons up to 90%), with a low cetane number and high nitrogen and sulfur contents (Lee et al., 2016, 2017a; Shin et al., 2017; Oh et al., 2019; Laredo et al., 2021). On the other hand, benzene, toluene, and xylene (BTX) are the basic raw materials in the chemical industry, and demand for them has been increasing (Lee et al., 2017b, 2018; Wu et al., 2018a; Chen et al., 2021). Therefore, converting the LCO through the hydrocracking process to BTX has significant economic benefits (Kim et al., 2017; Laredo et al., 2017, 2018).

Owing to the complexity of the components of LCO, tetralin is often used as a model compound of LCO to study the reaction mechanism and catalyst performance in the hydrocracking of LCO (Laredo et al., 2017; Lee et al., 2016). Although the hydrocracking process of tetralin to BTX includes many reactions, such as hydrogenation/dehydrogenation, isomerization, and alkylation (Chen et al., 2021), the whole reaction can be simplified to series reactions: tetralin is hydrocracked to BTX firstly, and then the BTX is further hydrocracked to gas components. BTX is the intermediate product of the series reactions, and the further hydrocracking of the BTX will reduce the selectivity of BTX.

The selectivity of BTX in the hydrocracking reaction can be increased by the use of "correct" catalysts (Lee et al., 2017a, 2018; Shin et al., 2017; Kim et al., 2020; Oh et al., 2020). A bifunctional catalyst with metal centers and acidic centers is widely used in the hydrocracking process. The metal center usually includes one or two types of elements from the group of Ni, W, Co, and Mo (Chen et al., 2021; Laredo et al., 2021), and Beta zeolites are proven to have excellent acid centers for hydrocracking catalysts due to their unique pore structure and acid properties (Kim et al., 2017; Lee et al., 2017a, 2018; Oh et al., 2020). However, the acidic sites on the external surface of the zeolite easily increase the carbon deposition of the catalyst (Wu et al., 2018b; Goodarzi et al., 2020; Le et al., 2022). Furthermore, they also strengthen the metal-acid interaction of the hydrocracking catalyst, thus increasing the hydrogenation activity of metal to deep hydrogenation of target products (Lee et al., 2017a; Wu et al., 2020).

The acid sites on the external surface of the zeolite, provided by the framework or extra-frame-work Al atoms (Shamzhy et al., 2019), can be reduced by selective removal of Al atoms from the external surface of the zeolite (Zhang et al., 2018; Bukhtiyarova

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et al., 2020). In this work, the Al atoms on the external surface of Beta zeolites were selectively removed through partial removing the templating agent in the zeolites during calcination combining with acid washing. Subsequently, the hydrocracking catalysts were prepared by loading WO₃ onto the Beta zeolites using the wettingimpregnation method and their catalytic performance for tetralin hydrocracking reaction was investigated.

2. Experimental section

2.1. Chemical materials

The chemicals used in this study were tetraethylammonium hydroxide (TEAOH, 35 wt%), solid silica gel (SiO₂, 98 wt%), sodium aluminate (Al₂O₃, 41 wt%), sodium hydroxide (NaOH, 96 wt%), tetralin (C₁₀H₁₂, 97 wt%), cyclohexane (C₆H₁₂, 99.9 wt%), carbon disulfide (CS₂, 99.9 wt%), ammonium chloride (NH₄Cl, 99.5 wt%), hydrochloric acid (HCl, 36–37 wt%), and ammonium metatungstate [(NH₄)₆W₇O₂₄·6H₂O, 97%].

2.2. Preparation of hydrocracking catalyst

2.2.1. Preparation of parent Beta zeolite

The detailed procedures to prepare the Beta zeolite were described in our previous work (Wu et al., 2018a). The molar ratio of the precursor mixture gel for preparation of the Beta zeolite was 4.9 NaOH: 40 SiO₂: 1 Al₂O₃: 8 TEAOH: 300 H₂O. The gel was stirred at room temperature for 2 h and then transferred to a stainless-steel reactor for the hydrothermal process at 140 °C for 48 h. The product (Na-form Beta zeolite) was centrifuged and washed with the deionized water several times and then dried overnight at 120 °C. Fig. S1 shows the XRD pattern of the parent Beta zeolite, a pure BEA structure with high crystallinity was detected, and other physical and chemical properties are close to those reported in the literatures (Kamimura et al., 2011; Ikuno et al., 2015).

2.2.2. The procedures of selective dealumination and conventional dealumination of Beta zeolite

(1) Selective dealumination

The detailed procedures of selective dealumination are as follows. First, the parent Beta zeolite was calcined at different temperatures for 180 min, and the calcination temperature includes 300 °C, 325 °C, 350 °C, 375 °C, 400 °C, 450 °C and 550 °C. The photopictures of Beta zeolites calcinated at different temperatures are shown in Fig. S2. It can be seen that, the color of Beta zeolites changes from white for parent (un-calcined) Beta zeolite to dark for unfully calcined Beta zeolites, and finally to white again when the templating agent was completely removed from the Beta zeolites after calcination at 550 °C. The carbon content in the Beta zeolites of different calcination degrees was determined using a highfrequency infrared carbon and sulfur analyzer (HIR-94B, Wuxi High-Speed Analytical Instrument Co., Ltd., China). The relative carbon content was calculated as the ratio of the carbon content of calcined Beta zeolites to that of the uncalcined Beta zeolites, and the results are shown in Fig. 1. The relative carbon content in calcined Beta zeolites decreased with the increase of calcining temperature, indicating that the content of templating agent in Beta zeolites can be controlled by adjusting the calcination temperature. The carbon content in the fully calcined Beta zeolites was decreased to less than 1.0 wt%, suggesting that the most templating agent in the Beta zeolites was removed through calcination at 550 °C for 180 min.



Fig. 1. The relative carbon content of Beta zeolites after calcination at different temperatures.

dealuminated by the hydrochloric acid treatment. 10 g of Beta zeolites was added to 100 g 1 mol/L hydrochloric acid solution, and the treatment was carried out at 80 °C for 8 h under stirring. After the treatment, the Beta zeolites were centrifuged, washed with deionized water several times, and dried overnight at 120 °C. The bulk SiO₂/Al₂O₃ of all Beta zeolites are shown in Table S1.

Finally, all the Beta zeolites were further calcined at 550 °C for 300 min to completely remove the templating agent, and then the fully calcined Beta zeolite was treated with 1 mol/L NH₄Cl solution at 90 °C for 3 h to replace the Na⁺ with H⁺. The ion-exchange process was repeated to remove the Na⁺ ions completely from the Beta zeolites. Thus, the H-form Beta zeolite was obtained.

(2) Conventional dealumination

The conventional dealumination of Beta zeolites was performed through fully calcining the Beta zeolites and then acid-treating them. A series of Beta zeolites were prepared by the conventional dealumination, and the acid treatment conditions and the bulk SiO₂/Al₂O₃ of Beta zeolites are shown in Table S2. In order to study the difference in the physicochemical properties and in the catalytic performance of the Beta zeolite prepared by the two dealumination methods, two groups of Beta zeolites with the bulk SiO₂/Al₂O₃ being 30 or 60 were characterized and used to prepare the hydrocracking catalysts. These Beta zeolites were named as SDA-X and CDA-X. The "SDA" and the "CDA" in the Beta zeolite's name represent the selective dealumination and the conventional dealumination respectively, and X represents the bulk SiO₂/Al₂O₃ of the Beta zeolites.

2.2.3. Preparation of Beta zeolite-supported WO₃ catalyst

The hydrocracking catalyst was prepared by the impregnation method, which was previously reported by our research group (Wu et al., 2018a, 2020). The procedures were as follows. Firstly, Beta zeolites were impregnated with the appropriate amount of ammonium metatungstate solution (25 wt%) and then dried at room temperature for 24 h. Secondly, the dried Beta zeolite solid was calcined at 550 °C for 180 min to obtain Beta zeolite-supported WO₃ catalysts for hydrocracking reactions. The catalysts are named by putting W in the front of their Beta zeolite samples, such as W/ CDA.

2.3. Characterization of the samples

The structure and crystallinity of all Beta zeolites were characterized by the X-ray diffraction method (XRD Bruker D8 Advance). The morphology and particle size of the Beta zeolites were observed and measured using scanning electron microscopy (SEM; FEI Ouanta200F) with a voltage of 20 kV. The bulk SiO₂/Al₂O₃ of the Beta zeolites was measured by the X-Ray Fluorescence (XRF) spectrometer (Axiosm AX). Before the measurement, the Beta zeolites were ground and mixed with boric acid and then tableted at the sample to boric acid mass ratio of 1:2. The acid property of the Beta zeolites was characterized by the temperature-programmed desorption of ammonia (NH₃-TPD), and the procedures of the NH₃-TPD were as follows. First, 500 mg of the Beta zeolites (20–40 mesh) was placed in a guartz tube, which was then placed in a furnace at 600 °C. The Beta zeolites were treated in the N₂ atmosphere for 30 min to remove the adsorbed substances. Then, the temperature was lowered to 120 °C, and NH₃ was purged into the tube for 30 min. Finally, the Beta zeolites were heated to 600 °C at a rate of 10 °C/min to desorb the NH₃, and the acid properties of the Beta zeolites were obtained by detecting the desorbed NH₃ with TCD. The specific surface area and pore volume of the Beta zeolites were measured by the low-temperature nitrogen adsorption and desorption method using the ASAP2010 BET analyzer (Micromeritics, USA). Beta zeolites were treated at 350 °C for 5 h before testing. The specific surface area of the Beta zeolites was calculated using the BET equation, the micropore volume was calculated by the t-Plot method, and the mesopore volume was calculated by the BJH method. The surface SiO₂/Al₂O₃ and binding energy (between metal and support) of the catalysts were analyzed using X-ray photoelectron spectroscopy (XPS; ESCALAB 250). The carbon content of the catalysts was measured using an infrared highfrequency carbon-sulfur instrument (HIR-94B; Wuxi High-Speed Analytical Instrument Co., Ltd., China), and the operating conditions were with the high-purity oxygen carrier gas, the combustion temperature of 1500 °C, frequency of 20 MHz, and the combustionsupporting agent of tungsten particles. WS₂ crystals in the catalyst were studied with transmission electron microscopy (TEM, FEI Tecnai G2F20), the calculation of the average number of layers and length of stacks is described in Wu et al. (2018a). The Al coordination state of Beta zeolites was studied by ²⁷Al MAS NMR with an instrument model Bruke-400 and an instrument frequency of 104 MHz, using Al(NO₃)₃ as a reference sample. Hydrogen temperature-programmed reduction (H₂-TPR) measurement of the catalysts was carried out on a self-built instrument. First, 30 mg of catalyst was treated at 500 °C for 2 h under argon (Ar) atmosphere and the temperature was reduced to 100 °C. Then, the gas atmosphere was switched to a mixed gas containing H₂/Ar (the volume ratio of H₂ was 6%), and the temperature was increased to 950 °C at a rate of 10 °C/min. A TCD detector was used to detect the content of hydrogen consumed in reduction.

2.4. Catalytic performance test of catalysts

2.4.1. Tetralin hydrocracking experiments

The hydrocracking reaction of the tetralin was carried out in a fixed-bed microreactor to determine the catalytic performance of the prepared catalysts. Before being used in the reaction, the catalyst was first sulfided with a cyclohexane solution containing 1.5 wt% CS₂ to reduce the WO₃ to WS₂. The conditions for sulfidation of the catalyst were as follows: weight hourly space velocity (WHSV) of 5 h⁻¹; the volume ratio of H₂ to cyclohexane solution of 1300:1; the pressure of 6.0 MPa; the temperature of 320 °C; and the sulfidation reaction time of 180 min. After the sulfidation of the catalysts, the tetralin was pumped into the fixed-bed microreactor.



Fig. 2. The surface ${\rm SiO}_2/{\rm Al}_2{\rm O}_3$ of selectively dealuminated and conventionally deal-uminated Beta zeolites.

The reaction conditions for hydrocracking of tetralin were as follows: 480 °C, 6 MPa, and the volume ratio of H₂ to tetralin of 1300:1. The catalytic performance of the catalysts at the WHSV between 3 h^{-1} and 8 h^{-1} was investigated.

2.4.2. Analysis of the liquid product

The liquid product of the tetralin hydrocracking reaction was collected and analyzed by SP3420 chromatograph (Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd., China) equipped with a flame ionization detector. The column of the chromatogram was the PONA column (50 m \times 0.2 mm \times 0.5 µm). The conversion of tetralin, BTX yield, and gas yield were defined by the following three equations, respectively.

$$\text{Conversion} = \left(\frac{W_{\text{Tetralin},0} - W_{\text{Tetralin},t}}{W_{\text{Tetralin},0}}\right) \times 100\% \tag{1}$$



Fig. 3. XRD patterns of selectively dealuminated and conventionally dealuminated Beta zeolites.



Fig. 4. NH₃-TPD profiles of selectively dealuminated and conventionally dealuminated Beta zeolites.

Table 1

The specific surface area and pore volume of selectively dealuminated and conventionally dealuminated Beta zeolites.

Samples	S _{BET} , cm ² /g	S _{micro} , cm ² /g	V _{total} , cm ³ /g	V _{micro} , cm ³ /g
CDA-30	559.1	445.4	0.50	0.25
SDA-30	567.0	471.8	0.48	0.23
CDA-60	547.9	428.1	0.56	0.21
SDA-60	525.0	394.7	0.61	0.19

BTX Yield =
$$\left(\frac{W_{\text{BTX}}}{W_{\text{Tetralin},0}}\right) \times 100\%$$
 (2)

Gas Yield =
$$\left(1 - \frac{W_{\text{Out}}}{W_{\text{Tetralin},0}}\right) \times 100\%$$
 (3)

where $W_{\text{Tetralin},0}$ is the mass of tetralin in feedstocks, $W_{\text{Tetralin},t}$ is the mass of tetralin in the product, W_{BTX} is the mass of BTX, and W_{Out} is



Fig. 6. ²⁷ Al MAS NMR of selectively dealuminated and conventionally dealuminated Beta zeolites.

the mass of the liquid product.

3. Results and discussion

3.1. Physical and chemical properties of Beta zeolites

Firstly, the surface SiO₂/Al₂O₃ of the selectively dealuminated and conventionally dealuminated Beta zeolites was measured by XPS (Luo et al., 2021), and the results are shown in Fig. 2. It can be seen that the surface SiO₂/Al₂O₃ molar ratios of selectively dealuminated Beta zeolites of the same bulk SiO₂/Al₂O₃ are higher than conventionally dealuminated Beta zeolites, indicating that the selective dealumination mainly removed Al from the external surface of Beta zeolites because the templating agent in center of Beta zeolite crystals hindered the internal dealumination of Beta zeolites. In contrast, because the templating agent was fully removed from the Beta zeolites, the Al was removed uniformly from all over the Beta zeolite crystals by the conventional dealumination method.



Fig. 5. N₂ adsorption/desorption isotherms (a) and pore size distribution (b) of selectively dealuminated and conventionally dealuminated Beta zeolites.

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Secondly, the structure and crystallinity of all Beta zeolites were characterized by the X-ray diffraction method and the XRD patterns of the selectively dealuminated and conventionally dealuminated Beta zeolites are shown in Fig. 3. All the Beta zeolites still were of a typical BEA topology, and the positions of their characteristic XRD peaks were almost unchanged at 2θ of 7.6°, 21.3°, and 22.4° (Apelian et al., 1996), this indicates that selective dealumination and conventional dealumination did not severely disrupt the crystal form of Beta zeolites. Similarly, it can be seen from Fig. S3 that no significant changes were found in the morphology of all the Beta zeolites after the selective dealumination and conventional dealumination, which confirms that dealumination under the conditions of this study has no effect on the morphology of Beta zeolites. The acid properties of the dealuminated Beta zeolites were measured by the NH₃-TPD, and the results are shown in Fig. 4. It can be seen that the acid amount and acid strength of the selectively dealuminated Beta zeolites were similar to those of the conventionally dealuminated Beta zeolites with the same bulk SiO₂/Al₂O₃.



Furthermore, the specific surface area and pore volume of the Beta zeolites were measured and are listed in Table 1. It can be seen from Table 1 that the specific surface area and pore volume are not very different for CDA-30 and SDA-30. With the deepening of dealumination, in comparison with CDA-30 and SDA-30, the specific surface area of the Beta zeolites (CDA-60 and SDA-60) decreased slightly and their pore volume increased slightly due to the collapse of a small part of the Beta zeolite framework during the dealumination process. The N₂ adsorption-desorption isotherms and pore size distribution of the selectively dealuminated and conventionally dealuminated Beta zeolites are shown in Fig. 5. It can be seen from Fig. 5a that the curves of all samples are of the same type, indicating that the pore types of the Beta zeolites prepared by the two methods are the same.

Finally, to further investigate whether or not the dealumination processes changed the structure of Beta zeolites, the ²⁷Al MAS NMR spectra of the dealuminated Beta zeolites were determined and the results are shown in Fig. 6. The peaks at 0 ppm and 55–60 ppm are



Fig. 7. XPS patterns of W/Beta catalysts.

assigned to octahedral coordination of typical extra-framework Al and the tetrahedrally coordinated framework Al (Wang et al., 2018), respectively. It can be seen from the figure that no extra-framework Al is observed, and only framework Al was contained in all samples, indicating that both selective dealumination and conventional dealumination did not change the Al environment. This further proved that the crystal structure of Beta zeolite was almost not changed by the dealumination processes.

3.2. Physical and chemical properties of W/Beta catalyst

To investigate the interaction of acid-metal sites in hydrocracking catalysts, XPS analysis of oxidized metals in catalysts was performed, and the results are shown in Fig. 7. It can be seen from Fig. 7 that the W4f spectra in all catalyst samples split into two peaks, attributed to W4f_{5/2} and W4f_{7/2} (Wu et al., 2020), respectively. Meanwhile, as the Beta zeolite bulk SiO₂/Al₂O₃ increases, W4f_{5/2} and W4f_{7/2} are shifted toward lower binding energies, indicating decreased metal-acid sites interaction force. On the other hand, the binding energy of SDA-60 was lower than that of CDA-60 samples, indicating that high surface SiO₂/Al₂O₃ decreases the metal-acid sites interaction.

WS₂ crystals in the catalyst were studied and recorded by transmission electron microscopy (TEM, FEI Tecnai G2F20), the calculation of the average number of layers and length of stacks is described in Fig. S4 and Table 2. It can be seen that the average stacking layers and length of WS₂ increase as the SiO₂/Al₂O₃ increases. The average stacking layers and length of the selectively dealuminated Beta zeolites were larger than those of the conventionally dealuminated Beta zeolites, suggesting that the high surface SiO₂/Al₂O₃ in Beta zeolites can increase the average stacking layer number and length of WS₂. Besides, owing to metal reducibility depending on the metal-acid interaction force, H₂-TPR analysis was used to evaluate the reducing ability of hydrocracking catalysts, and the results were shown in Fig. 8. It can be seen that the H₂ consumption of all W/Beta starts from around 450 °C. However, the peak position of the highest peak of the selectively dealuminated Beta zeolites shifts to high temperature compared to conventionally dealuminated Beta zeolites under the same bulk SiO₂/Al₂O₃ ratio, indicating a decrease in reducing ability. This is because the metal-acid sites interaction force and the metal agglomerated of the selectively dealuminated Beta zeolites decreased (Wan et al., 2009.).

3.3. Catalytic performance of WO₃/Beta catalyst

The hydrocracking reaction of tetralin is composed of a series of complex parallel and consecutive reactions (Sato et al., 1999, Laredo et al., 2018). The main reaction network consists of two types of hydrocracking reactions: tetralin hydrocracking to BTX (reaction rate constant was denoted as k_1) and BTX further deep hydrocracking to light alkanes (reaction rate constant was denoted as k_2). For this two-step series reaction, the yield of intermediates (BTX) increases as the value of k_1/k_2 raises.

Hydrocracking catalysts were prepared by loading WO₃ onto the

Table 2	
Average length and stacking layers of WS ₂ in the catalys	st.

Sample	L, nm	Ν
W/CDA-30	6.14	3.11
W/SDA-30	6.56	3.30
W/CDA-60	7.05	3.91
W/SDA-60	7.43	4.04

Beta zeolites, and the hydrocracking of tetralin to BTX was used to study the effect of the changes of surface SiO₂/Al₂O₃ on their hydrocracking catalytic performance. The conversion of tetralin, BTX yield, gas yield etc. are shown in Fig. 9. It was difficult to distinguish the activity and selectivity of the different hydrocracking catalysts when the conversion of tetralin was 100% at the low WHSV (less than 3 h⁻¹ from Fig. 9a) (Wu et al., 2020). Therefore, the WHSV was chosen to be 3-8 h⁻¹ to obtain the different conversion of the catalysts.

As shown in Fig. 9a, the conversion of the conventionally dealuminated Beta samples is higher than selectively dealuminated samples whether the bulk SiO₂/Al₂O₃ is 30 or 60. Furthermore, the BTX yield of the selectively dealuminated Beta samples is higher than that of the conventionally dealuminated Beta samples at the same bulk SiO₂/Al₂O₃ as seen from Fig. 9b. These phenomena demonstrated that, compared with conventionally dealumination, selectively removing of external surface acid sites of Beta zeolites has weakened the hydrocracking activity (both k_1 and k_2 are decreased). This is because Beta zeolite prepared by selective dealumination has weaker acid-metal interaction than Beta zeolite prepared by conventional dealumination, which has higher hydrogenation activity (verified by H₂-TPR results). It is easy to be seen from Fig. 9b and d that, the BTX yield of the selectively dealuminated Beta zeolites is higher than that of the conventionally dealuminated Beta zeolites at the same bulk SiO₂/Al₂O₃, which means the value of k_1/k_2 of selectively dealuminated Beta samples is higher than that of conventionally dealuminated Beta samples. Therefore, selectively removing of external surface acid sites can decrease the hydrogenation rate of BTX more than decrease the hydrocracking rate of tetralin.

It is generally accepted that the deactivation of hydrocracking catalysts is usually caused by coke deposited on the catalysts, and low pressure and low hydrogen to oil ratio could induce fast catalyst deactivation (Chen et al., 2021). Therefore, in order to investigate the coking performance of the selectively dealuminated and conventionally dealuminated Beta zeolites, the amount of coke deposited on the prepared catalysts was investigated under low pressure and hydrogen to oil ratio (The pressure was 1 MPa, the volume ratio of H_2 and tetralin was 325:1), and the results are shown in Fig. 10. It can be seen that, under the same reaction



Fig. 8. H₂-TPR profiles of W/Beta catalysts.

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Fig. 9. Catalytic performance of selectively dealuminated and conventionally dealuminated Beta zeolites. (**a**) Conversion of tetralin, (**b**) BTX yield, (**c**) Gas yield, (**d**) Relationship between the gas yield and the BTX yield. Evaluating conditions: reaction temperature was 480 °C, the pressure was 6 MPa, the volume ratio of H₂ and tetralin was 1300:1.

conditions and the same time on stream, the amount of coke deposited on W/CDA-30 and W/SDA-30 zeolites is significantly larger than that of W/CDA-60 and W/SDA-60, owing to the more acid sites of W/CDA-30 and W/SDA-30 than W/CDA-60 and W/SDA-60. In addition, for the same bulk SiO₂/Al₂O₃, the amount of coke deposit on the selectively dealuminated Beta zeolites was lower than that of the conventionally dealuminated Beta zeolites, indicating that the coke deposit is more likely to form on the external surface of the Beta zeolite. It was reported that the coke deposit precursor in the LCO hydrocracking process is mainly polycyclic aromatic hydrocarbons (PAHs) (Gutiérrez et al., 2012). Therefore, coking reaction is more likely to occur on the external surface of Beta zeolite due to the large size of PAHs molecules.

In order to investigate the location of carbon deposition in the catalysts, the specific surface area and pore volume of the fresh and deactivated catalysts prepared from W/CDA-30 and W/SDA-30 were measured, and the results are shown in Table S3. It can be seen from the table that the micropore loss of the catalyst prepared by W/CDA-30 is 54.6%, while the micropore loss of the catalyst prepared by W/SDA-30 was only 25.6%. Therefore, it shows that the carbon deposition of the catalyst prepared by W/CDA-30 is mainly located on the external surface of Beta zeolite, which leads to pore blocking, while the selective removal of Al content on the external surface of the catalyst (W/SDA-30) effectively reduces the occurrence of pore blocking (Fogassy et al., 2011.).



Fig. 10. Carbon content of catalysts prepared by selectively dealuminated and conventionally dealuminated Beta zeolites.

Evaluating conditions: the reaction temperature was 480 °C, the pressure was 1 MPa, the volume ratio of H_2 and tetralin was 325:1, the WHSV was 5 h^{-1} , the reaction time on stream was 24 h.

4. Conclusion

Beta zeolites were selectively dealuminated through partially removing templating agent used for the preparation of the Beta zeolites by calcination and then treating them with acid solution. It was shown that, for the same bulk SiO₂/Al₂O₃, Beta zeolites dealuminated with the selective dealumination had higher surface SiO₂/Al₂O₃ than that of Beta zeolites dealuminated with conventional dealumination, while their morphology, acid properties, pore structure, and Al coordination status were like each other. The hydrocracking catalysts were prepared by loading metallic component WO₃ on the prepared Beta zeolites, and their catalytic performance was tested using tetralin hydrocracking to prepare BTX as the probe reaction. The catalytic performance testing experiments showed that the catalysts based on the selectively dealuminated Beta zeolites had higher BTX selectivity and lower coke formation rate than that the catalysts based on the conventionally dealuminated Beta zeolites.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petsci.2022.10.015.

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