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Highly active BEA catalyst for catalytic cracking of *n*-heptane

Ryosuke Nakao[a], Yoshihiro Kubota[b], Naonobu Katada[c], NorikazuNishiyama[d], Kimio Kunimori[a],
and Keiichi Tomishige[a,]*

[a]*Institute of Materials Science, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8573, Japan*
[b]*Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan*
[c]*Department of Materials Science, Faculty of Engineering, Tottori University, 4-101 Koyama Minami, Tottori 680-8552, Japan*
[d]*Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*

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Homemade BEA(HTS) catalysts prepared by the hydrothermal synthesis method exhibited much higher activity than commercial BEA, USY and ZSM-5 in catalytic cracking of *n*-heptane. It is characteristic that BEA(HTS) has a much larger amount of Brönsted acid sites than other zeolites. This is related to the high activity.

KEY WORDS: catalytic cracking; *n*-heptane; BEA zeolite; deactivation; regeneration.

1. Introduction

The fluid catalytic cracking (FCC) process has been one of the most important processes in petroleum refining. The process can contribute to the conversion of heavy gas oils and resid fuels to gasoline, diesel fuel, and light gases. The ratio of heavy oils in the petroleum will become higher in the future. This is why the FCC process is expected to be more important. In the 1970s, ultrastable Y-zeolite (USY) was applied to the FCC process, and the catalyst is one of the main components in current practical FCC catalysts. Novel catalysts are necessary to meet requirements of next-generation refineries whose productions can conquer environmental issues and the changing demand of the market [1]. Especially, in the FCC process, the subject is to increase the yield of gasoline, which is a most useful product. An effective method for higher gasoline yield is the short contact time (SCT) of catalyst/oil. This is because SCT can decrease cracking to gas and polymerization of produced olefin. In the conventional FCC reactor, the riser system has been adopted. In order to realize the SCT condition, a down-flow system is being developed [2,3]. However, in the SCT operation, the reduced catalyst/oil contact time leads to lower intrinsic conversion and bottoms cracking [4]. In order to keep the high conversion under the SCT condition, highly active catalysts are necessary. The activity of FCC catalysts is much dependent on the strength and amount of acidity; furthermore, high ability of reactant diffusion is also important. In terms of these points, USY is regarded as one of the suitable catalysts since the strong acidity is formed by the interaction between Brönsted acid sites and extra-framework Al species, and it has a lot of mesopores [5,6]. On the other hand, we have tested novel beta zeolites (BEA) by hydrothermal synthesis, because it has been known that BEA is a zeolite containing a 3D system of large pores circumscribed by a 12-member ring, possessing stronger acidity than conventional USY [7,8]. In addition, it is easy to form small crystal BEA, according to the previous report [9]. In this study, the catalytic cracking of *n*-heptane was carried out as a model reaction of FCC under the condition close to a practical one including regeneration steps. In addition, the catalyst performance of homemade BEA was compared with those of the various commercial catalysts (BEA, USY, ZSM-5). Furthermore, the catalysts were characterized by X-ray diffraction, N2 adsorption, temperature-programed desorption (TPD) of NH_3 adsorption, and FTIR spectra of pyridine adsorption. The relation between the catalyst performance and characterization results is discussed in the following section.

2. Experimental

2.1. Catalyst preparation and characterization

Homemade BEA zeolite synthesized by the hydrothermal method (HTS) [10] is denoted as BEA(HTS). A typical synthetic procedure of the BEA(HTS) is as follows: 31.56 g (75.0 mmol) of 35 wt% tetraethylammonium hydroxide ($TEA + OH^-$, Aldrich) solution and 32 wt% NaOH (5.63 g, 45.0 mmol) were mixed with stirring. After the stirring was continued for 15 min, 22.53 g (150 mmol) of colloidal silica (Ludox HS-40, Du Pont) was added and the mixture was stirred for another

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* To whom correspondence should be addressed.
E-mail : tomi@tulip.sannet.ne.jp

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30 min. To the homogeneous mixture, a solution of $Al_2(SO4)_3$ (1.69 g, 4.97 mmol) in 16.2 g of deionized water was added; the gel was further stirred for 4 h. The mixture was then transferred to a 125-mL Teflon-lined autoclave. Afterwards, the autoclave was kept statically in a convection oven at 448 K for 3 days and then cooled to room temperature. The crystals obtained were filtered, washed several times with deionized water, and dried overnight to give 9.49 g of white powder, which was identified as BEA by powder X-ray diffraction (XRD-6000, Shimadzu) with Cu Kα radiation. To remove the structure-directing agent (SDA) occluded inside the zeolite pore, the as-synthesized zeolite was placed in a muffle furnace and heated stepwise in a flow of air (flow rate = 50 mL/min). The temperature was raised from room temperature to 813 K over a period of 7 h, and then kept at the same temperature for 4 h, and finally the sample was cooled to room temperature in ambient condition. The conversion of the sodium type to ammonium type was carried out as follows: the sodium type sample was put into an aqueous solution of ammonium nitrate ([NH4]/[Na] = ca. 10), stirred at 348 K for 4 h, and filtered. These were twice repeated and the obtained solid was dried at 373 K for more than 10 h in air. BEA(HTS) was stored in the ammonium type. In the activity test of cracking of *n*-heptane, other commercial proton-type zeolites were used for the comparison: H-BEA(Tosoh), H-BEA(PQ), H-USY(Tosoh), and H-ZSM-5(Tosoh). These zeolites were supplied from companies that are indicated in parentheses. All of the catalysts were pressed, crushed, and sieved to 150–250-mm granules. The properties of the catalysts are listed in table 1. The crystal structure was analyzed by powder X-ray diffraction (XRD-6000, Shimadzu) with Cu Kα radiation. Surface area and porosity measurements were carried out by means of nitrogen adsorption on a Belsorp 28SA apparatus (Bel Japan). The acidity of the catalysts was measured by TPD of NH_3 adsorption according to the water vapor treatment method [11,12]. A sample of 0.1 g was packed into the quartz cell installed in a TPD equipment (TPD-AT-1(NH_3), Bel Japan Inc.) and evacuated at 773 K for 1 h. Ammonia (13.3 kPa) was introduced into the cell and the pressure was kept at 373 K for 30 min. After evacuation for 30 min, water vapor (about 3 kPa) was admitted into the cell and exposed to the sample for 30 min at 373 K. Evacuation and addition of water was repeated twice. The sample was heated at the heating rate of 10 K/min in flowing the carrier helium at 0.044 mol/s and the pressure in the catalyst bed was 13.3 kPa. The desorbed ammonia was detected by a quadruple mass spectrometer (ANELVA M-QA 100F). After the measurement, a known concentration of ammonia was fed into the mass spectrometer in order to calibrate the desorption peak intensity. The amount of ammonia was determined on the basis of the intensity of the fragment with $m/e = 16$ because the parent peak ($m/e = 17$) was influenced by the desorbed water.

Table 1
Catalyst properties of various BEA zeolites

Sample	Si/Al_2	SA ($m^2 g^{-1}$)	V_t ($mL g^{-1}$)
BEA(HTS)	27	581	0.22
BEA(Tosoh)	27	560	0.21
BEA(PQ)	25	538	0.23

Note: SA: specific surface area; V_t: total micropore volume given by *t*-plot methods.

The FTIR spectrum was collected in a transmission mode using a sample disk (10 mg, 1 cm in diameter) set in an *in situ* cell. The sample disk was evacuated at 873 K for 1 h, followed by the adsorption of pyridine vapor (ca. 400 Pa) at 373 K for 30 min, and further evacuation at 573 K for 1 h. The spectrum was collected with an FTIR spectrometer (FT/IR-5300, Jasco).

2.2. Activity test of catalytic cracking of n-heptane

The catalytic cracking of *n*-heptane was carried out in a continuous-flow fixed-bed reactor at 773 K. Nitrogen was used as a carrier gas. Catalyst weight was 0.050 g. The total pressure was 0.10 MPa. The flow rate of carrier gas was 3.3 mmol/min and that of *n*-heptane was 0.033 mmol/min. A syringe pump (100DX-S, ISCO Inc.) was used for the feeding of *n*-heptane. Each catalyst was pretreated in a nitrogen stream at 873 K for 1 h. Ammonium ions are present on BEA(HTS) before the pretreatment; however, almost all the ammonia is desorbed, which is supported by TPD of NH_3, as shown below. After this pretreatment, the catalyst was cooled down to the reaction temperature, 773 K, in the carrier gas. In the activity test of *n*-heptane cracking, the reaction was carried out for 45 min. In the case of the FCC process, zeolite catalysts were deactivated because of coke deposition. For the catalyst regeneration, the deposited coke is removed by the combustion with air. Therefore, after 45-min activity test, the catalyst was regenerated in flowing dry air (50 cm^3 STP/min) for 20 min at 923 K. The cycle of reaction–regeneration was repeated three times. The cracking products were analyzed by a gas chromatograph (GC-17A, Shimadzu) equipped with an FID detector using a capillary column (RTX-1, PONA). The products were methane, ethane, ethylene, propane, propylene, *n*-butane, *iso*-butane, olefins of C4 components, and traces of C5, C6, and other oligomerization components. The conversion of *n*-heptane is calculated by the equation:

$$(n\text{-heptane conversion }(\%)) = 100\left[1 - \frac{(n\text{-heptane in effluent (mol)})}{(n\text{-heptane in feed (mol)})}\right]$$

3. Results and discussion

Figure 1 shows the results of the activity test in the catalytic cracking of *n*-heptane over various catalysts. After the regeneration, all the catalysts regained their activity to the extent of the fresh ones. It is very interesting that BEA(HTS) exhibited much higher initial activity than other zeolites. The order of initial activity was as follows: BEA(HTS) $\gg$ ZSM-5 (Tosoh) > BEA (PQ) > BEA(Tosoh) > USY(Tosoh). Catalyst deactivation was observed significantly over BEA(HTS); however, this can be due to high conversion of *n*-heptane. Except over ZSM-5, catalyst deactivation was more or less clearly observed. This behavior has been reported previously [13]. More significant deactivation was observed over the catalyst with higher activity [14]. Figure 2 shows the product distribution of cycle I in figure 1 over BEA(HTS). The main products were C3 and C4 hydrocarbons. The ratio of paraffin to olefin (P/O ratio) in the products decreased with time on stream. In the yield of C3 hydrocarbon, the tendency is more significant. These profiles can be due to the higher conversion of olefins to coke at a shorter reaction time. After the reaction of cycle I, the amount of coke over BEA(HTS) was estimated to be 23 mg/g-cat, which was obtained from the weight loss during air flowing, using the thermogravimetric analysis. Catalyst activity could be recovered by a regeneration process over various catalysts. The order of initial activity did not agree with that of acid amount (BEA(HTS) $\gg$ USY(Tosoh) > ZSM-5(Tosoh) > BEA(Tosoh) > BEA (PQ)) listed in table 2.

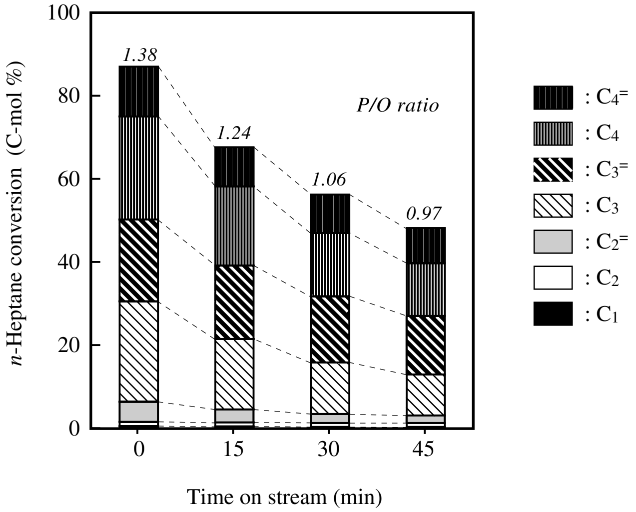

Figure 2. Product distribution in *n*-heptane cracking over BEA(HTS) within cycle I in figure 1. A ratio of paraffin/olefin (P/O ratio) in the products is also shown.

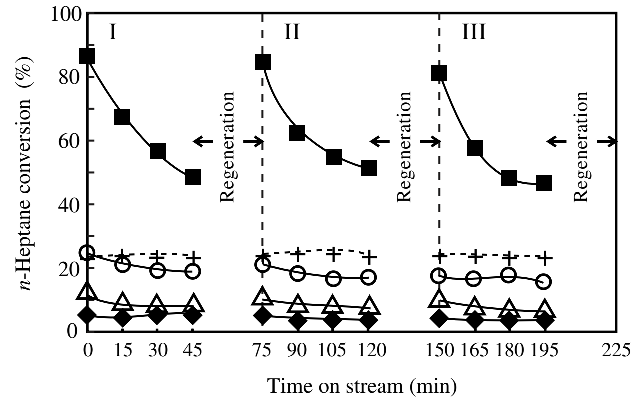

Figure 1. Results of the activity test in *n*-heptane cracking. Effect of time on stream and regeneration. (■) BEA(HTS); (△) BEA(Tosoh); (○) BEA(PQ); (◆) USY(Tosoh); (+) ZSM-5(Tosoh). Reaction conditions: reaction temperature 773 K; total pressure 0.10 MPa; the flow rate of N_2 3.3 mmol/min; the flow rate of reactant gas 0.033 mmol/min. Regeneration conditions: dry air flowing 50 cm^3/min at 923 K for 20 min.

XRD patterns of BEA zeolites are shown in figure 3. XRD patterns of homemade BEA(HTS) (calcined sample) were almost the same as those of commercial BEA zeolites. Specific surface areas (SA) and total pore volumes (V_t) were obtained using the BET and *t*-plot method respectively on the basis of the nitrogen adsorption isotherms. The values are listed in table 1. From this comparison, the surface area and pore volumes of BEA(HTS) were not so different from those of other BEA zeolites. Acidic properties of catalysts can be characterized by TPD spectra of NH_3. Figure 4 shows the TPD spectra of samples. In addition, the acid amounts of zeolites, which are estimated on the basis of TPD spectra, are listed in table 2. In figure 4, the desorption peak at about 470 K (l-peak) is assigned to a weakly adsorbed NH_3, which is adsorbed on the very weak acid site owing to the octahedral Al ion, which is not in the zeolite framework. Peaks at the higher temperature of about 600 K (*h*-peak) and about 800 K (h^+-peak) are ascribed to acid sites. Especially, the *h*-peak can be assigned to the acid site formed by Al in the zeolite lattice structure. On the other hand, the h^+-peak can be assigned to the interaction between the Al ion in the framework and the octahedral Al ion [15]. The acid amount of the h^+-peak is much smaller than that of the *h*-peak. From the position of the peak top of the *h*-peak, the order of acid strength is as follows: ZSM-5 > BEA(HTS) > USY(Tosoh) > BEA(Tosoh) @ BEA (PQ). From the ammonia TPD spectra shown in figure 4, the number and strength of acid sites were determined (table 2). Average adsorption heat, i.e., an index of acid strength, was determined from the position, shape, and intensity of the highest peak according to the curve-fitting method [11]. The heats of BEA and USY samples were similar, whereas that of the ZSM-5 was high. The acid amount on BEA(HTS) was much larger than that on other catalysts. Figure 5 shows FTIR spectra of pyridine adsorbed on BEA zeolites. Peaks at 1545 cm^{-1} and 1455 cm^{-1} are assigned to the pyridinium ion adsorbed on Brönsted acid sites and the pyridine coordinated to Lewis acid sites respectively [16–18]. In

Table 2
Acidic properties of various zeolites

Sample	Si/Al_2	[Al] ($mol\,kg^{-1}$)	A_{acid} ($mol\,kg^{-1}$)	A_{acid} / [Al]	DH0 ($kJ\,mol^{-1}$)
BEA(HTS)	27	1.03	0.96	0.93	128
BEA(Tosoh)	27	1.14	0.58	0.51	124
BEA(PQ)	25	1.23	0.51	0.41	126
USY(Tosoh)	6.3	4.01	0.70	0.17	131
ZSM-5(Tosoh)	22	1.39	0.67	0.48	137

Note: A_{acid} is estimated from the $h + h^+$ peak in TPD spectra in figure 4. ΔH_0 is the average heat of ammonia adsorption from the position, shape, and intensity of the highest peak according to the curve-fitting method [11].

the case of BEA(Tosoh) and BEA(PQ), the peak area of $1545\,cm^{-1}$ was much smaller than that of $1455\,cm^{-1}$. This indicates that the amount of Brönsted acid sites was rather small, while the amount of Lewis acid sites was large. Generally speaking, Lewis acid sites are considered to be formed by some extra-framework Al ions, which are formed by dealumination or the hydrothermal synthesis process. However, other extra-framework Al ions do not work as acid sites. Therefore, the ratio A_{acid}/[Al] is usually lower than 1. In the case of commercial BEA zeolites, the ratio A_{acid}/[Al] was much lower than 1. In contrast, the ratio A_{acid}/[Al] on BEA(HTS) was larger and close to 1 (table 2). Moreover, in the FTIR spectra, the peak area of $1545\,cm^{-1}$ on BEA(HTS) was much larger than that on BEA(Tosoh) and BEA(PQ). These indicate that almost all the Al atoms on BEA(HTS) form acid sites more effectively. Comparison of these results with acidic properties suggests that the higher cracking activity of *n*-heptane over homemade BEA(HTS) is related to a larger amount of acid sites and their strong acidity.

4. Conclusions

Homemade BEA zeolite prepared by hydrothermal synthesis exhibited much higher activity in catalytic cracking of *n*-heptane than various commercial catalysts (BEA, USY, ZSM-5). The deactivation over BEA(HTS) was severe because of high activity; however, the activity was recovered almost completely by the regeneration process. From the characterization of acidic properties,

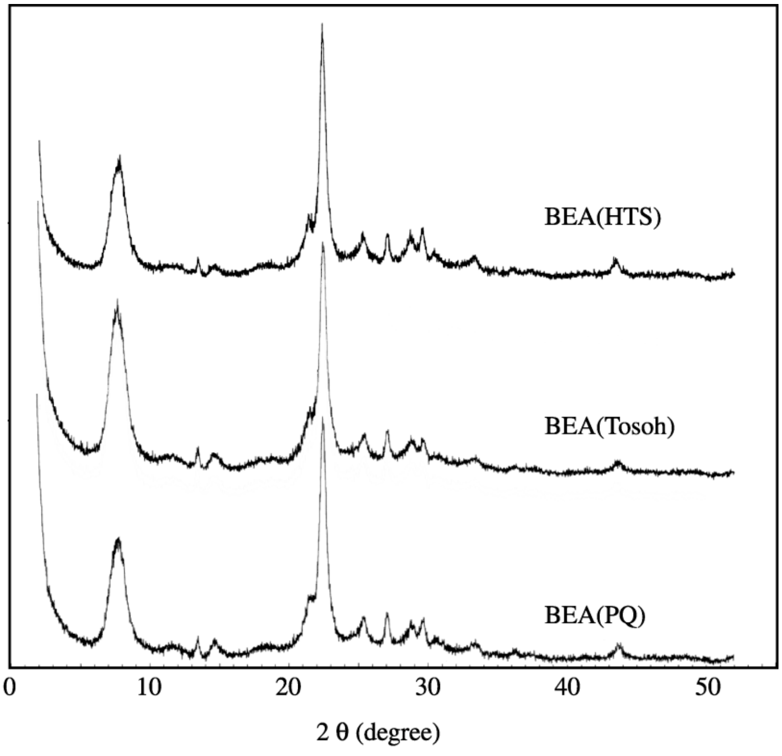

Figure 3. XRD spectra of BEA zeolites. X-ray Source: Cu Kα.

it is found that acid sites are formed effectively and the amount of acid sites is significantly large over BEA(HTS). Furthermore, the ratio of Brönsted acid sites to Lewis acid sites was much higher on BEA(HTS) than on commercial BEA zeolites. This character on BEA(HTS) can explain the cause of highly active BEA in the catalytic cracking of *n*-heptane.

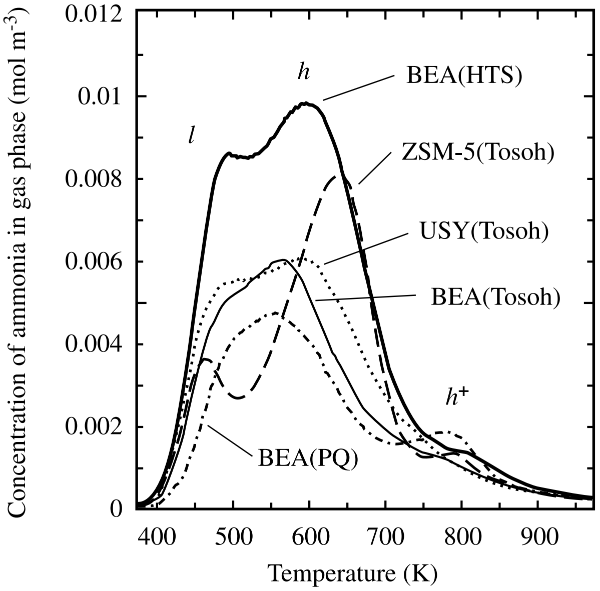

Figure 4. NH_3 TPD spectra measured by water vapor treatment method: NH_3 adsorption: 13.3 kPa, 373 K, 30 min; pretreatment evacuation: 773 K, 30 min; sample weight: 0.1 g; water vapor treatment: ~ 3 kPa, 373 K, 30 min; heating rate: 10 K/min.

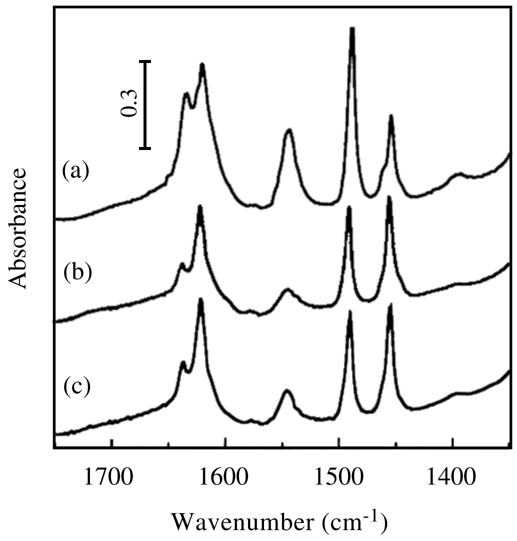

Figure 5. FTIR spectra of pyridine adsorbed on beta zeolites. (a) BEA(HTS), (b) BEA(Tosoh), and (c) BEA(PQ) Pretreatment evacuation: 873 K for 1 h, pyridine adsorption: 373 K, 400 Pa; evacuation after the pyridine adsorption: 573 K for 1 h; sample weight: 10 mg.

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