Preparation and activity evaluation of Y zeolites with or without mesoporosity

Koichi Sato [a,b], Yoichi Nishimura [b] and Hiromichi Shimada [b]

[a] *Advanced Catalysts Research Laboratory, Tsukuba Blanch, Petroleum Energy Center, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*
[b] *National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

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The primary purpose of the present study was to elucidate the role of mesopores of Y zeolites in the hydrocracking of large molecules, such as heavy oils. For this purpose, two kinds of HY zeolites, one with and one without mesopores, were prepared by ion exchange of two NaY zeolites with different Si/Al ratios. Their catalytic activities were then evaluated by the hydrocracking of two model compounds, each having a different molecular size. In the hydrocracking of diphenylmethane, which has a smaller molecular size and thus can diffuse into micropores, the two HY zeolites exhibited similar catalytic activities. On the other hand, in the hydrocracking of triphenylmethane, which has a larger molecular size, the HY zeolite with mesopores gave almost four times higher reaction rates as compared with the HY zeolite without mesopores. This higher activity was because the larger molecular size limits the catalytically active sites to those only on the external surface including the mesopore surface of the HY zeolite particles. These results indicate that the catalytic activities over the total surface and over the external surface can be estimated using two model reactions, each involving a compound that has a different molecular size.

Keywords: Y zeolite, hydrocracking, mesopore, external surface, crown ether template

1. Introduction

Proton-exchanged faujasite-type (HY) zeolites with high Si/Al ratios are extensively used as catalysts in fluid catalytic cracking (FCC) and hydrocracking of petroleum feedstocks. When a HY zeolite is used in heavy oil cracking, particularly when used as a hydrocracking catalyst, diffusional limitation of large molecules in micropores of HY zeolites is a serious and unavoidable problem; namely, the catalytically active sites of HY zeolites are limited to the external surface of the particles, including the mesopore surface. Therefore, formation of mesopores as well as dealumination are critical for improving the catalytic performance of HY zeolites that in nature have low mesoporosity and low Si/Al ratios.

During the formation of mesopores, the crystal structure of HY zeolites is destroyed, in particular the external surface of the particles becomes nearly amorphous [1]. This destruction presumably leads to catalyst deactivation and also makes it difficult to clarify the correlation between the catalytic activities and properties of HY zeolites. Due to these ambiguities, there have been relatively a small number of papers that discuss the detailed properties on HY zeolites as compared with ZSM-5 or mordenite zeolites having rigorous flame structures. In particular, very few studies have been performed on the roles of mesopores of HY zeolites in spite of their practical importance.

Our final aim is to prepare HY zeolites with high crystallinity and large amounts of mesopores that are suitable for accommodating heavy feedstocks. For this purpose, a method must be established for preparing zeolites with mesoporosity and for correctly evaluating their catalytic activities. In this study, two kinds of HY zeolites, one with and one without mesoporosity, were prepared by ion-exchange treatments of two different NaY zeolites that have different Si/Al ratios. After detailed characterization of the physical properties, the hydrocracking activities of the two HY zeolites were evaluated by hydrocracking two model compounds that had different molecular sizes. The properties and activities of a rare-earth-exchanged Y-zeolite (RE-Y) catalyst were also examined as a typical cracking catalyst that is commercially used. Comparing the characterization and reaction results of the three zeolites, the role of mesopores in the hydrocracking was discussed.

2. Experimental

2.1. Preparation of the catalysts

Two kinds of NaY zeolites were used as starting materials: NaY(TO) with a bulk Si/Al ratio of 2.9 (Tosoh Corporation); and NaY(CE) with a bulk Si/Al ratio of 3.6 prepared by hydrothermal synthesis according to a previously described method [2] in which 15-crown-5 was used as a template. The HY zeolites were obtained by ion exchange using an aqueous solution of $(NH_4)_2SO_4$ (3 mol/l) at 368 K for 1 h, followed by drying at 393 K for 12 h and calcining in dry air at 873 K for 3 h. This ion-exchange cycle was repeated three or four times, until the final Na concentration was below 0.6%. The total amount of $(NH_4)_2SO_4$ in the ion-exchange solution was 1.7 eq for the first cycle, and 3.0 eq for the later cycles. A RE-Y zeolite (Catalysis and Chemicals Industries Co., Ltd., or CCIC) was chosen as a reference to commercial cracking catalysts.

2.2. Measurement of the physical properties and chemical composition of the catalysts

The porosity of each zeolite was determined by measuring the N_2 isotherm at 77 K with a Micromeritics ASAP 2010 system. The X-ray diffraction (XRD) patterns were recorded with a MAC Science MXP-18 diffractometer and Cu Kα radiation. The relative crystallinity was estimated by comparing the peak intensities of six XRD peaks assigned to (331), (511), (440), (533), (642), and (555) reflections. The unit cell parameters were calculated from the (533) and (642) reflection peak positions that were determined using the (101) reflection peak of TiO_2 (anatase) as an internal standard. The framework Si/Al ratio was obtained from the unit cell parameters by using Breck's equation when the Si/Al was smaller than 3 [3], and by using Engelhardt's relation when the Si/Al was larger than 3 [4]. The bulk Si/Al ratio was determined by inductively coupled plasma analysis (ICP), and the Na concentration by atomic absorption analysis. The morphology of particles was examined by using a Hitachi S-800 scanning electron microscope (SEM).

The acid strength distribution was measured by using the NH_3-TPD method (NH_3 temperature-programmed desorption) and a BEL-Japan TPD-1S system with a quadrupole mass spectrometer. After being pre-heated at 773 K under a He flow, the sample was treated with a flow of 10% NH_3/He for 20 min. After the removal of physisorbed NH_3 by evacuation at 373 K for 1 h, the TPD spectrum was obtained by heating the sample from 373 to 973 K at a heating rate of 10 K/min under a He flow.

2.3. Model reactions

For the model compounds of different molecular sizes, we used 5.4% triphenylmethane (TPM; Wako Pure Chemical Industries, Ltd., purity $>98\%$) and 10.9% diphenylmethane (DPM; Nacalai Tesque Inc., purity $>99\%$) solutions (with the balance being *trans*-decalin (Wako Pure Chemical Industries, Ltd., purity $>99\%$)). These reagents were used without further purification. The minimum molecular size of TPM is ca. 11.9 Å (determined by MOPAC calculation), and that of DPM ca. 6.2 Å. The model test reactions were carried out by using a 35 ml batch-type reactor that had an electric furnace and a rocking system. The experimental conditions were as follows: 10 ml of model solution, 0.1 g of dried catalyst, initial hydrogen pressure of 5.9 MPa (cold charge), reaction temperature of 573 K, and a reaction time between 5 and 60 min. Before all the reactions, the catalysts were dried in air for 2 h. The products and reactants were analyzed using gas chromatography with FID detector (Hewlett–Packard 6890) employing methylsilicon capillary columns (Hewlett–Packard #1, 0.20 mm × 25 m). It was confirmed that the amounts of the impurities in the reactants and their products were negligible.

3. Results and discussion

3.1. Characterization of the prepared Y zeolite samples

Table 1 shows the physical properties and chemical compositions of the zeolite samples. Both of the HY zeolites had high XRD crystallinity. This precludes significant destruction of zeolite framework structure during the ion-exchange and calcination treatments. For both of the HY zeolites, the SEM pictures in figure 1 show no changes in the physical appearance of the particles during these treatments. The particle sizes of Y(CE) were larger than those of Y(TO) (figure 1).

For both of the HY zeolites, the ion-exchange and the following calcination treatments reduced the unit cell parameters that correspond to dealumination from the framework (table 1). In contrast to the increasing Si/Al ratios of the framework, the bulk Si/Al ratios of the zeolites measured by ICP were not significantly changed by the ion exchange. This is likely due to the presence of non-framework aluminum oxide species or isolated Al in HY

Table 1
Characterization of catalysts.

Catalyst	Surface area (m^2/g)		Pore volume (ml/g)		Relative crystalinity[c] (%)	Dealumination[d] (%)	Unit cell dimension (Å)	Si/Al molar ratio		Na content (wt%)
	Micropore	External[a]	Micropore[a]	Mesopore[b]				XRD	ICP	
NaY(TO)	753	46	0.330	0.068	100	0	24.63	2.81	2.90	7.09
HY(TO)	644	122	0.299	0.114	80	35.8	24.52	4.95	3.18	0.27
NaY(CE)	755	38	0.334	0.015	124	0	24.57	4.07	3.63	6.14
HY(CE)	623	58	0.292	0.026	101	19.5	24.50	5.30	3.69	0.56
RE-Y	707	38	0.286	0.043			24.67	2.47	2.57	0.16

[a] t-plot measurement.

[b] Calculated by the BJH method using the N_2 desorption isotherm.

[c] NaY(TO) = 100%.

[d] Na form standard.

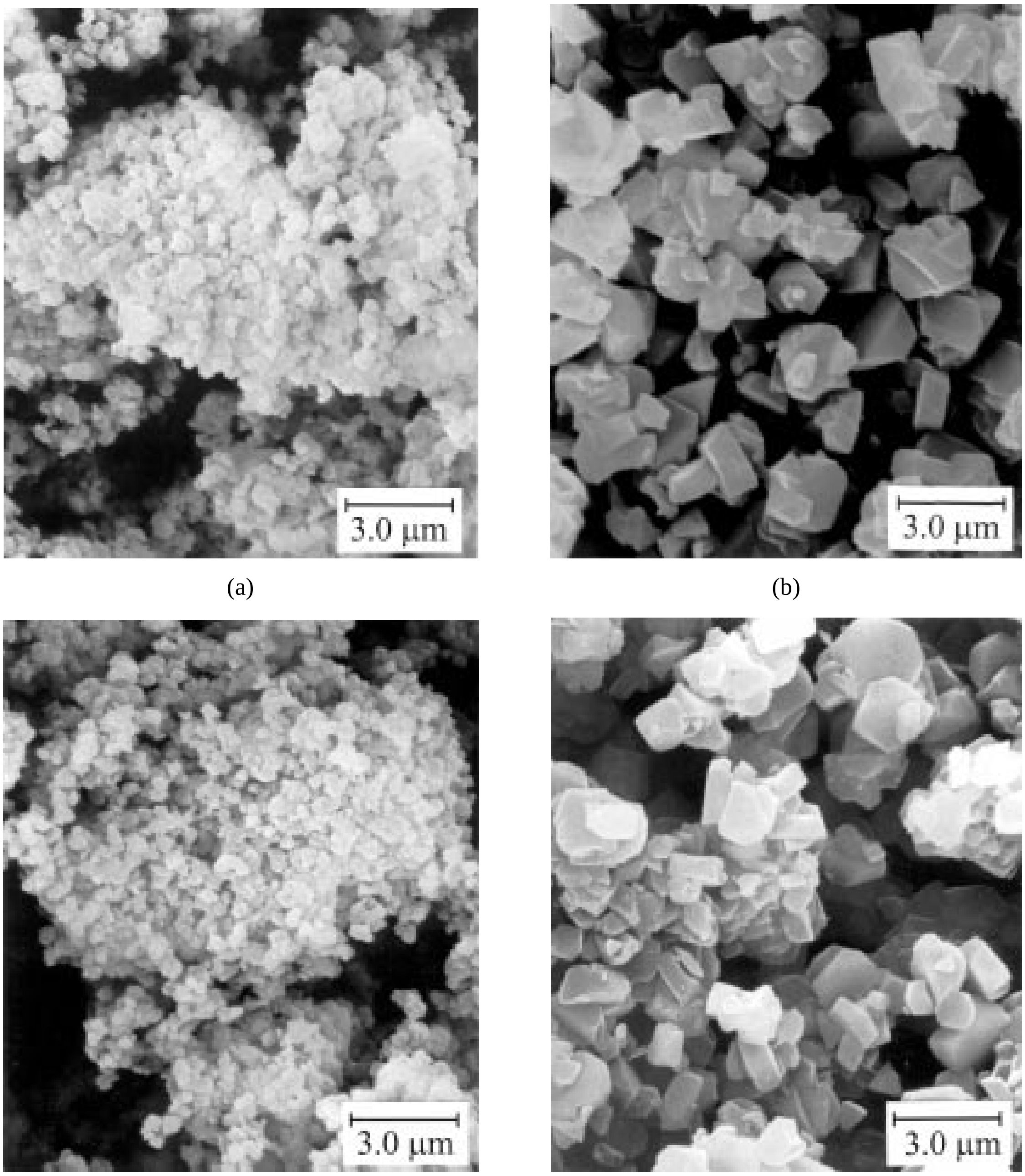

Figure 1. SEM images (magnification ×5000) of the Y zeolites before and after ion-exchange treatment: (a) NaY(TO), (b) NaY(CE), (c) HY(TO), and (d) HY(CE).

zeolites [5] and is consistent with the slight decreases in the crystallinity.

Four cycles of ion exchange were required to reduce the Na concentration of Y(CE) below 0.6 wt%, whereas only three exchanges reduced the Na concentration of HY(TO) to 0.27 wt% (table 1). This indicates that Na ion exchange as well as dealumination from Y(CE) are slower than those from Y(TO).

After the ion-exchange treatment, the changes in and values for the surface area and pore volume of micropores for Y(TO) were similar to those for Y(CE). About a 10% decrease in the volume of micropores caused by ion exchange can be attributed to the collapse of the zeolite crystalline structure and might be due to the presence of amorphous Al_2O_3. On the other hand, the external surface area and mesopore volume of HY(TO) were significantly larger than those of HY(CE). These results confirm that ion exchange increases the mesoporosity of HY(TO).

The pore size distributions differed among the HY zeolites (figure 2). The profile of HY(TO) shows the presence of mesopores with an average diameter of 40 Å, in contrast to the very small mesopore volume in HY(CE). In summary, the Na ion exchange and calcination treatments cause dealumination from both Y(TO) and Y(CE) without significant collapse of micropore structure. Dealumination with mesopore formation from Y(TO) proceeds more easily than that from Y(CE). These observations, indicating a rigorous frame structure for Y(CE) during the ion-exchange and calcination treatments, are consistent with a previous result by Lohse et al., who reported little formation of mesoporosity in Y-zeolites prepared using crown ether after steaming at 773 K [6]. Thus, production of mesopores is related to the chemical composition of the starting NaY zeolite, that is, the framework Si/Al ratio. Ion-exchange and steaming treatments result in dealumination with framework vacancies. The vacancies grow by interconnections among themselves through the transport of Si, and finally form mesopores [7,8]. High Si/Al framework ratios of Y(CE) zeolites hinder the interconnection of vacancies, because the number of Al in each unit cell is small.

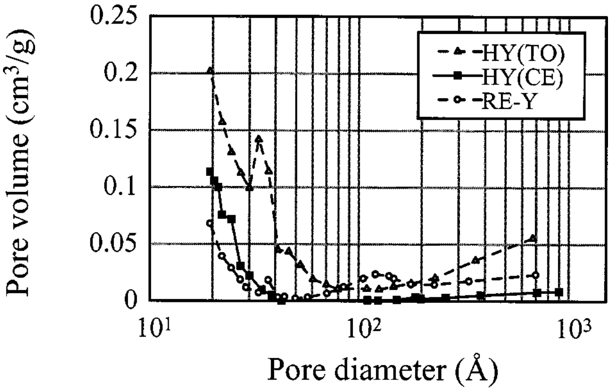

Figure 2. Pore size distribution of Y zeolites calculated by the BJH method using the N_2 desorption isotherm.

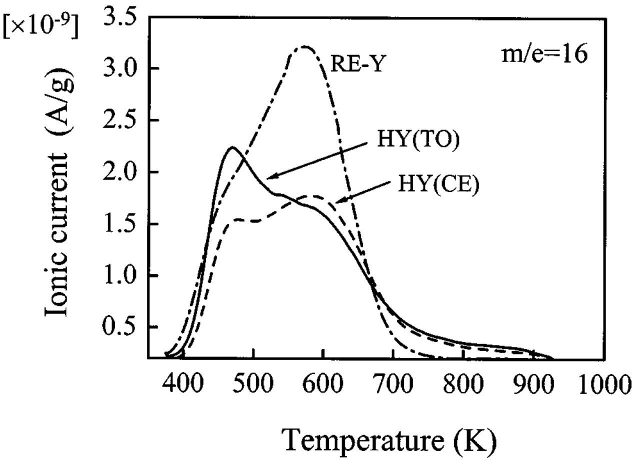

Figure 3. NH_3-TPD profiles of Y zeolites.

The NH_3-TPD spectra (figure 3) show that RE-Y had a significantly higher number of acid sites than did the two HY zeolites, and that, although the acid strength distributions slightly differed, HY(TO) and HY(CE) had similar numbers of acid sites.

The above results indicate that the microporosity, chemical composition, and acidity of HY(TO) arising from the zeolite framework are similar to those of HY(CE). On the other hand, the mesoporosity is significantly different between the two HY zeolites.

3.2. Hydrocracking reaction of TPM and DPM

Figure 4 shows the conversions of DPM and TPM versus reaction time over the three zeolites. In both of the reactions, the conversions increased linearly with the reaction time at the very beginning, but the reaction rates rapidly decreased in very short periods. This catalyst deactivation is presumably due to the coke formation on the acid sites of the zeolites. To discuss the diffusion of the reactants in micro- and mesopores, the initial specific reaction rates over the catalysts were calculated using the conversions at the beginning of the reactions (table 2). HY(TO) and HY(CE)

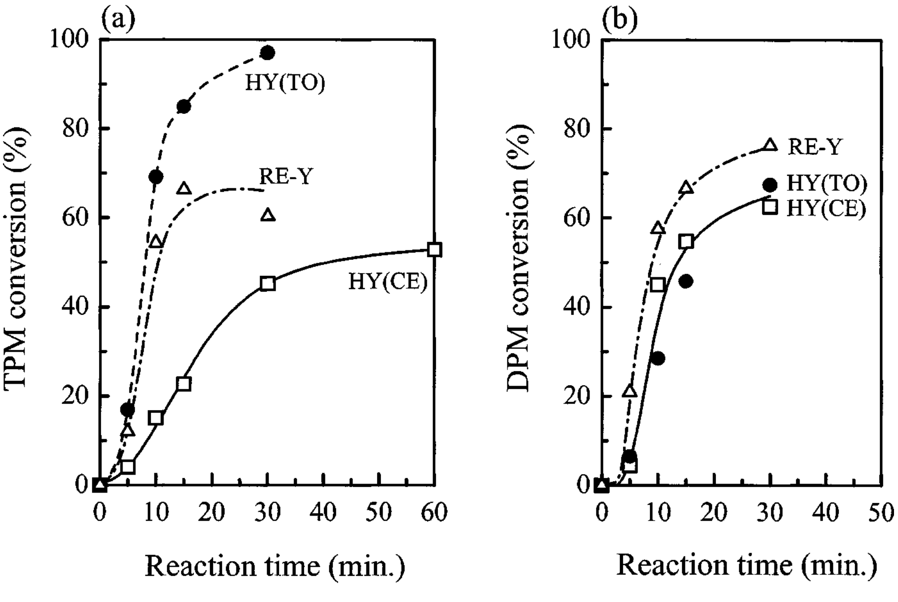

Figure 4. Feed conversion of hydrocracking model reaction using (a) TPM and (b) DPM.

Table 2
Specific reaction rates of DPM and TPM.

Catalyst	DPM rate per total surface area (mol/min m^2)	TPM rate (mol/min m^2)	
		Per total surface area	Per external surface area
HY(TO)	2.7×10^{-6}	2.3×10^{-6}	1.4×10^{-5}
HY(CE)	2.1×10^{-6}	6.2×10^{-7}	7.3×10^{-6}
RE-Y	8.8×10^{-6}	1.7×10^{-6}	3.3×10^{-5}

gave similar reaction rates per a total surface area in the reaction of DPM. The highest rate over RE-Y can be attributed to the largest number of acid sites, as evidenced in the NH_3-TPD spectra (figure 3). These indicate that almost all the acid sites, including those in the micropores, are accessible for DPM, which is sufficiently small to diffuse into the micropores of HY zeolites (7.4 Å).

In contrast to the reaction rate of DPM, that of TPM per a total surface area decreased in the order of HY(TO) $>$ RE-Y $>$ HY(CE). The rate of TPM over HY(TO) was almost four times as high as that over HY(CE). This indicates that the TPM cannot diffuse into micropores due to its large molecular diameter. Thus, the active sites for TPM are limited to the external surface, including the mesopore surface of the HY zeolites particles. The discrepancy in the order between the reaction rates for DPM and TPM is due to the presence or absence of mesopores.

When the reaction rates per an external surface area were compared, the rate over HY(TO) was still almost two times higher as compared with that over HY(CE). This may be due to an effect of a "specific field" provided by mesopores of HY(TO) that does not occur on the external surface of particles. It cannot be precluded that migrations of Na and Al during the ion-exchange and calcination treatments change the properties of the mesopore surface of HY(TO) or external surface of HY(CE) that effect the intrinsic catalytic activities. RE-Y showed a higher reaction rate than did HY(TO), probably due to the larger number of acid sites on the external surface of RE-Y.

These results indicate that TPM hydrocracking reflects the catalytic activity over the external surface including the mesopore surface of zeolites, whereas the DPM hydrocracking reflects that over the total surface. Therefore, by comparing the results of the two model reaction tests, we can evaluate catalytic activities over both the external and micropore surfaces. Note that amorphous SiO_2–Al_2O_3 catalysts show very low hydrocracking activity for DPM and TPM despite the large number of mesopores. Both mesopores and high crystallinity of zeolite structures are essential for high hydrocracking activity for large molecules.

4. Conclusion

We successfully prepared two HY zeolites that have a similar framework of chemical composition but have different mesopore structures. By conducting test reactions involving the two zeolites and two compounds that have different molecular sizes, we determined the catalytic activities over the total and mesopore surfaces. The results indicate that the mesopores of HY zeolites would play a crucial role in the hydrocracking of large-size molecules.

Acknowledgement

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