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Decrease of catalytic activity and solid acidity by ion exchange of Na cation on HZSM-5

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Abstract

Dependence of the cracking activity on solid acidity was studied on HZSM-5 with different concentrations of Na cation. The IR intensity of the hydroxide bond ascribable to Brønsted acid site decreased gradually with increasing degree of exchange of Na cations, and disappeared at an exchange degree of about 80%. Cracking of octane was studied in order to examine the dependence on the number of Brønsted acid site at 773 to 823 K. It was found that the rate of cracking was related to the number of Brønsted acid sites in a more than first-order dependence at 773 K, but was clearly first-order at 823 K. Therefore, the catalytic cracking activity of the HZSM-5 was simply related to the number of Brønsted acid sites only at high temperatures. The rate of cracking was related simply in a first-order with respect to the partial pressure of octane at a temperature as high as 823 K. Solid acidity as measured by temperature programmed desorption of ammonia could not be related simply to the catalytic activity, because the method could not discriminate between Lewis and Brønsted acid sites.

Keywords: Octane cracking; Solid acidity; HZSM-5; Brønsted acidity; Reaction mechanism

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1. Introduction

Catalytic cracking of hydrocarbons is a working reaction in the petroleum refinery process, and seems to be a simple reaction, but difficult problems about the reaction remain unsolved. In particular, there is still a controversy concerning the mechanism of cracking and the active acid site.

Lombardo et al. first reported an interesting experimental finding that the activity for cracking of neopentane was suppressed strongly by loading a small amount of a basic compound on HZSM-5 [1]. Only about 10% of the basic molecule per included aluminum atom was sufficient to inactivate the zeolite completely. They proposed some possible explanations for the finding, e.g. only a small portion of acid sites active for the reaction, a physical effect on the zeolite, etc. Baba et al. then studied this problem, and reported that the activity for cracking of hexane was deactivated by exchanging 50% of the protons for Na ions [2]. They proposed a long-range interaction among acid sites; in their proposed mechanism, the proton was regarded to be a mobile species, and only a small amount of Na cations disturbed the mobility completely. Their conclusion was also supported by their NMR study for the protons [3]. Kotrel et al. also studied this problem from a viewpoint of solid acidity, and found a strong relation between the activity and IR band intensity of Brønsted hydroxide on zeolites Y, β, and ZSM-5 [4].

In our previous study on zeolite acidity using temperature programmed desorption (TPD) of ammonia, we identified the acid site as simply related to the Al in the tetrahedral site of zeolite, and a 1:1 relation is clearly observed between the number of acid sites and the amount of Al–Na [5]. The acid sites on the NaH–zeolites behaved independently, and the long-range interaction between them was not confirmed. It is found in the recent study that the acidity of zeolite often changes depending on the procedure of preparation and the storage conditions. Particularly, the fully protonated form with a high concentration of Al is readily dealuminated by humidity [6]. This means that the zeolite acidity is not related to the chemical composition simply, and a comprehensive characterization of the acidity is required to understand solid acidity. In this study, therefore, we will study the decrease of the cracking activity with Na exchange level based on

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the careful characterization of the acid site in the HZSM-5 in order to determine the relationship between the catalytic activity and zeolite acidity.

2. Experimental methods

HZSM-5 was synthesized under hydrothermal conditions. Tetra-*n*-propyl ammonium bromide was used as an organic template. Ludox HS-40 (Dupont) was used as a silica source, and mixed with $Al_2(SO_4)_3$, NaOH and the organic template. The mixture was put into a Teflon-sealed autoclave, which rotated vertically at a rate of 16 rpm. The hydrothermal synthesis was carried out at 443 K for 72 h. After the synthesis, the obtained gel was thoroughly washed with de-ionized water, followed by drying overnight. In order to remove the organic template molecule, the sample set in a glass tube was calcined at 813 K in a flow of N_2 and O_2 mixture for 12 h. The sample thus produced was then ion-exchanged in a solution of NH_4NO_3 to finally obtain the NH_4-type ZSM-5. The NH_4ZSM-5 was ion-exchanged in a solution of NaCl to obtain the NaNH$_4$ZSM-5, where the concentration of NaCl was adjusted to obtain the degree of exchange of Na, 5–100%. The NaNH$_4$ZSM-5 was calcined in air to remove ammonia to obtain the NaH-ZSM-5.

The chemical composition of zeolite was measured using inductively coupled plasma (ICP) after digestion in HF; hereafter, the degree of Na ion exchange was shown as 100 × (Na/Al), as shown in Table 1.

A powder X-ray diffraction pattern was recorded by a Rigaku Miniflex Plus diffractometer with a 0.45 kW Cu Kα X-ray source (30 kV, 15 mA). Infrared spectra were collected on a self-supporting disk of 10 mm diameter molded from 10 mg of the zeolite powder in an in situ cell by a JASCO FT/IR-5300 spectrometer. ^{27}Al MAS NMR spectra were measured at 78.2 MHz with 5000 Hz spinning frequency and 1 μs pulse width, and scans were made 100 times at intervals of 5 s. Prior to the measurements, zeolite samples were stored in a container with water saturated with ammonium chloride for at least 48 h to fully adsorb water, because it was difficult to detect ^{27}Al MAS NMR spectra clearly under the dried conditions. TPD of ammonia was measured by commercially installed equipment (TPD-1-AT(NH_3), Bel Japan Inc.). The detailed procedure for the TPD experiment was described elsewhere [5].

Cracking of octane was performed using a continuous-flow technique. Nitrogen carrier gas (flow rate, 60 ml/min) was fed into liquid octane chilled with an ice bath or heated with water warmed at 313 K, and the vapor of octane was fed into the catalyst packed in a Pyrex glass tube reactor at 673 or 723 K. Products and octane were analyzed by gas chromatography (Shimadzu 14A) with a silicone capillary column and an FID detector directly through a sampling valve.

Table 1
Zeolite samples used in this study and the chemical composition of Al and Na

	Al (mol kg^{-1})	Na (mol kg^{-1})
NH$_4$ZSM-5 (3%)[a]	0.59	0.02
HZSM-5 (5%)	0.57	0.03
NaHZSM-5 (9%)	0.56	0.05
NaHZSM-5 (10%)	0.58	0.06
NaHZSM-5 (16%)	0.58	0.09
NaHZSM-5 (21%)	0.53	0.11
NaHZSM-5 (49%)	0.53	0.26
NaHZSM-5 (75%)	0.52	0.39

[a] Exchange degree of Na, shown in a parenthesis as (Na/Al) × 100%.

3. Results and discussion

3.1. Characterization

Chemical composition of the zeolites was measured by ICP, and the determined Na exchange degree is shown in Table 1. The NH$_4$ZSM-5 and HZSM-5 also contained a small amount of Na as an impurity. XRD of the samples was measured (not shown), and the structure of MFI was retained after the ion exchange.

^{27}Al MAS NMR was measured, as shown in Fig. 1. Signals at 55 and 0 ppm were ascribable to Al in the tetrahedral and octahedral configurations, respectively. The ratio of the two kinds of Al was not simply related to the degree of Na exchange. From the intensity, it was estimated that about 10% of Al existed out of the framework of zeolites. Some of the Al were therefore identified as dealuminated from the framework, during the steps of preparation and/or the ion exchange process. However, the NMR of ^{27}Al could not be

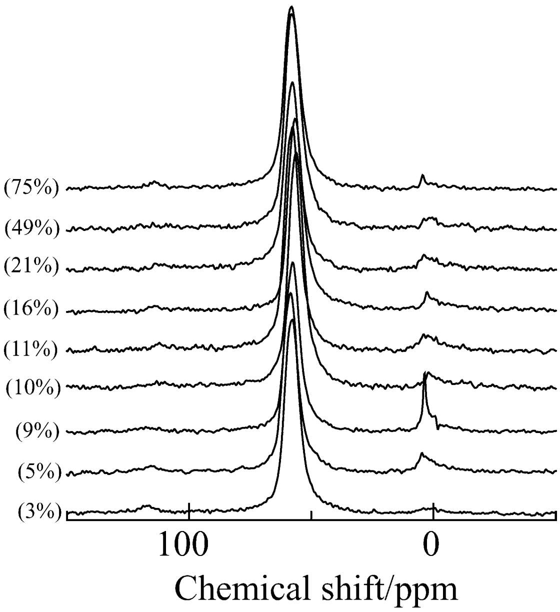

Fig. 1. ^{27}Al NMR of the samples containing the amount of Na cation shown in the parenthesis.

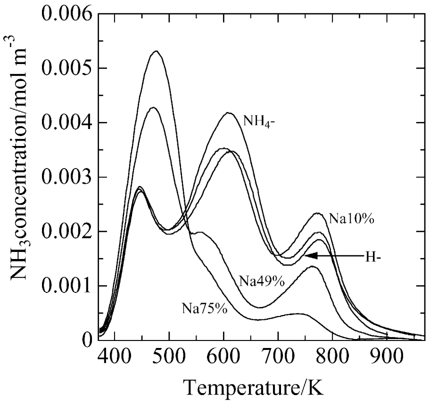

Fig. 2. TPD of ammonia on the samples, NH_4-, H-, Na (10%)-, Na (49%)-, and Na (75%)-HZSM-5.

used for the quantitative measurements, because it has been reported that some aluminum species was invisible by NMR spectroscopy.

TPD of ammonia was measured for the characterization of acidity. As shown in Fig. 2, TPD of ammonia on HZSM-5 showed three desorptions, and these were named *l*-, *h*-, and h^+-peaks at low, high and higher temperatures [7]. As previously identified, the *l*-peak is not ammonia directly adsorbed on the acid site, and the *h*-peak is ascribable to ammonia desorbed from the acid site. However, in this case, relatively large intensity was observed for the h^+-peak. A recent study on the identification of the h^+-peak has shown that it is either ascribed to the enhanced Brønsted acid site, or to acid sites that show strong acidity but are inactive for the reaction [7]. TPD of ammonia however cannot differentiate between these two possibilities.

Infrared spectroscopy of HZSM-5 showed that the hydroxide band at 3610 cm^{-1} is ascribable to the Brønsted acid site, as shown in Fig. 3. The integrated intensity was quantitatively measured, and plotted against the exchange level of Na, as shown in Fig. 4. The band intensity decreased gradually with increasing exchange level of Na, and disappeared at about 80%. Therefore, a non-linear dependence of the Brønsted acidity on the exchange level of Na cation was therefore confirmed.

Fig. 5 shows the plots of the TPD intensities of the *h*- and h^+-peak against the relative intensity of the Brønsted acid site as measured above. The peak intensity for the *h*-peak was linearly plotted against the Brønsted acid site, while the h^+-peak intensity was not. Therefore, the *h*-peak can be preferably regarded as the Brønsted acid site. However, the TPD experiment has shown the desorption of ammonia even on the zeolite without the hydroxide band at 3610 cm^{-1}. This would be understood either as the presence of the Lewis acid site to accommodate ammonia, or as the presence of extra-framework species such as alumina to retard the free vibration of OH bands. The extra-framework aluminum species and SiOH defect seems to be formed during the preparation procedure, resulting in affecting the inten-

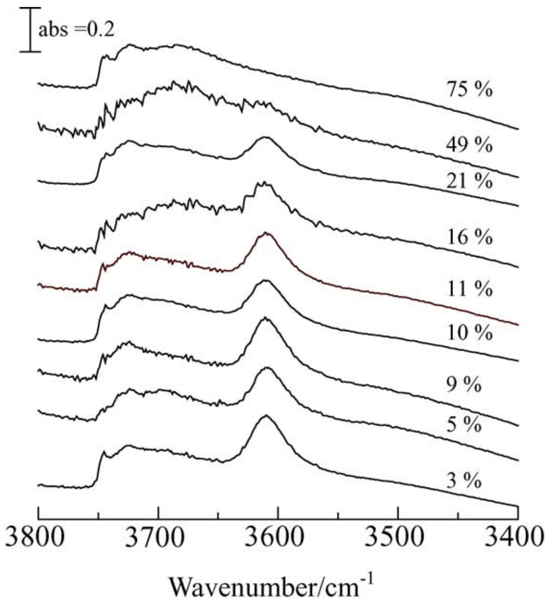

Fig. 3. Infrared spectra of the hydroxide band for the samples containing Na 3–75%.

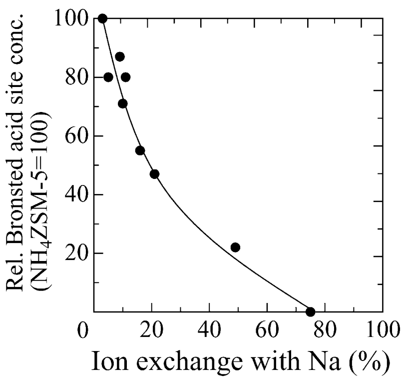

Fig. 4. Plot of the intensity of the Brønsted hydroxide band against the ion exchange level by Na cation.

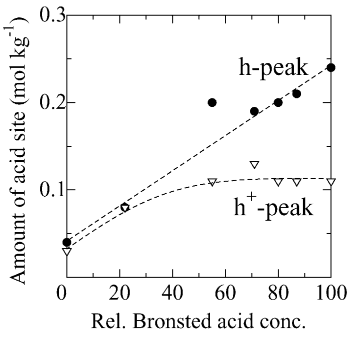

Fig. 5. Relation of the amount of acid sites found as *h*- and h^+-peaks in the TPD of ammonia to the relative intensity of the Brønsted acid site measured by IR spectroscopy.

sity of the Brønsted hydroxide band. However, at present, it is difficult to decide which mechanism should be accepted.

Using TPD of ammonia, the HZSM-5 prepared in this study has been characterized to be a material with complex acidity. In the following description, therefore, the relative IR intensity of the Brønsted hydroxide band will be correlated with the catalytic activity.

3.2. Dependence of the catalytic activity on the solid acidity

Catalytic activity of octane cracking was then measured using the continuous-flow method at conditions of different partial pressure of octane and temperatures of 673 and 723 K. The activity of the catalyst kept an almost constant level of conversion with time-on-stream. The conversion obtained at 15 min was therefore used to show the activity. Because the activity often exceeded 10%, the integrated rate equation was used to determine the rate constant.

The rate constant of octane cracking was measured using samples with different Na concentration at octane partial pressure of 266–3192 Pa. The rate constants measured at 673 and 723 K were shown in Fig. 6. Non-linear and linear relations were observed at 673 and 723 K, respectively. This means that the relationship of the rate constant with the Brønsted acid site depends on the temperature, and a simple linear relation is obtained at a high temperature such as 723 K.

Fig. 7 shows the plots of the rate constant against the partial pressure of octane using the same experimental data in Fig. 6. These mean that the rate of octane cracking has a first-order dependence with respect to partial pressure of octane at 723 K, but it has more than first-order dependence at 673 K. Therefore, the mechanism of cracking depends on the temperature of reaction.

From these experimental data, we can write the cracking rate equation with parameters of partial pressure P and concentration of the active site θ.

At 673 K, $r = kP^{m}(\theta)^{n}$, where $m, n > 1$

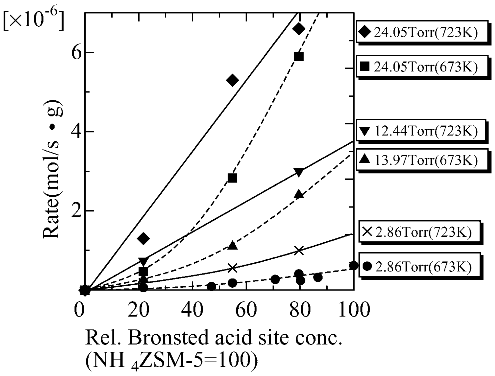

Fig. 6. Rate of octane cracking measured at 673 and 723 K by varying the partial pressure, plotted against the relative intensity of the Brønsted acid site.

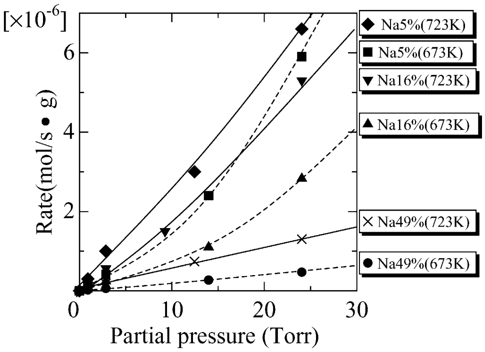

Fig. 7. Rate of octane cracking measured at 673 and 723 K on three kinds of NaHZSM-5, plotted against the partial pressure of octane.

At 723 K, $r = kP^{m}(\theta)^{n}$, where $m, n = 1$

Haag and Dessau reported that the mechanism of hydrocarbon cracking is dependent on the reaction temperature [8]. In this literature, the mechanism of cracking is divided into the monomolecular and bimolecular reactions at high and low temperatures, respectively. At relatively high temperature, the cracking proceeds in a monomolecular reaction mechanism through the formation of penta-coordinated carbonium ion. On the other hand, at low temperature, it proceeds via a bimolecular mechanism. The finding in the present study, therefore coincides well with the temperature-dependent mechanism, proposed by Haag and Dessau.

Kotrel et al. found a strong relationship between the activity for hexane cracking and the Brønsted OH intensity measured by IR on Y, β, and ZSM-5 zeolites. The present study agrees with their conclusion, and shows a more precise quantitative dependence of the activity on the Brønsted acidity, depending on the reaction temperature.

4. Conclusions

Based on the comparison between the catalytic activity and characterization data, the following conclusions can be drawn.

(1) Catalytic activity is related strongly with the Brønsted OH band intensity on the NaH-ZSM-5.
(2) The mechanism of catalytic cracking depends on the reaction conditions, and a simple first-order reaction occurs at a high temperature of 773 K, resulting in the simple correlation between the activity and acidity.
(3) Solid acidity measured by the TPD of ammonia is not simply related to the catalytic activity, but the *h*-peak intensity is more profoundly related to the catalytic activity of cracking.
(4) Careful consideration into reaction mechanism and zeolite characterization is required for understanding the catalytic cracking on zeolites.

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