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Phenol oxidation over alkaline earth metal ion exchange beta zeolite in the presence of ketone

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Abstract

The correlation between acid property of beta zeolite and its catalytic performance for phenol oxidation has been studied. Acid properties of beta zeolites in the proton form (H-BEA) and modified beta zeolite by alkaline earth metal ion exchange treatment (AE/H-BEA, AE: Mg, Ca, Sr, and Ba) were investigated by diffuse-reflectance FT-IR (DR-FTIR) spectroscopy. It was revealed that the features of the OH group stretching region of Ca/H-BEA are different from those of H-BEA. The peak at 3782 cm^{-1} observed on H-BEA disappeared and new peaks appeared at 3672–3692 cm^{-1} after the ion exchange treatment. NH_3 temperature programmed desorption analyses (NH_3-TPD) of these zeolites were also carried out. The NH_3 desorption peak at ∼873 K observed on H-BEA, which has been assigned to a very strong acid, disappeared, and a new peak at 743 K and a shoulder at the temperature lower than the peak at about 623 K appeared after the ion exchange treatment. These observations suggested that the acid properties of H-BEA were substantially modified by the ion exchange treatment. Phenol oxidation with hydrogen peroxide as oxidant over AE/H-BEA was conducted in the presence of diethylketone, and the result was compared with that over H-BEA. While the selectivity for diphenols, catechol and hydroquinone, over H-BEA based on added hydrogen peroxide was ∼89% that over AE/H-BEA was higher than 94%. The best catalyst was Ca/H-BEA, where the selectivity was as high as ∼98%. From these results, it is concluded that AE/H-BEAs are more suitable catalysts for the phenol oxidation with hydrogen peroxide than H-BEA, and it is suggested that the removal of strong acid sites by the ion exchange treatment would be the reason for their high selectivity.
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Keywords: Beta zeolite; H-BEA; Acid property; Alkaline earth metal ion exchange; Phenol oxidation; Hydrogen peroxide

1. Introduction

Hydrogen peroxide has been regarded as a clean oxidant because the oxidation reaction with hydrogen peroxide affords only water as by-product. Phenol oxidation into diphenols, catechol and hydroquinone, with hydrogen peroxide as oxidant is a typical industrial oxidation process (Scheme 1).

The products of this process are now widely used as starting materials for medicines, perfumes, and many other fine chemicals, and therefore the phenol oxidation process is industrially important. Usually, the phenol oxidation is catalyzed by acid and inorganic acids such as sulfuric acid and perchloric acid have been used as catalysts in the industrial process. However, in these processes a very large amount of by-products such as tar is produced, and a portion of hydrogen peroxide is consumed non-selectively. Thus, the product yield is not sufficiently high in these processes. In addition, acid catalysts such as sulfuric acid have to be finally neutralized and discarded. Therefore, despite of the versatile usability of hydrogen peroxide as oxidant, the industrial phenol oxidation process could not be regarded as a green process as yet. In order to expedite a real green phenol oxidation process, development of further active and selective oxidation catalysts is required.

We are now developing a catalytic system based on zeolite as solid acid. In our previous paper, we have reported that beta zeolite in the proton form (H-BEA) shows high catalytic performance for the phenol oxidation with hydrogen peroxide as an oxidant in the presence of diethylketone [1]. In this

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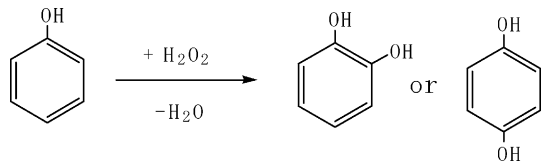

Scheme 1. .

paper, we will report on the catalytic performance of AE/H-BEA, which was obtained by treating H-BEA with alkaline earth metal ions. Correlation between catalytic performance and the acidic property will be studied on these zeolites.

2. Experimental

H-BEA (Zeolyst, SiO_2/Al_2O_3 = 75) was used after calcination at 823 K in air for more than 2 h. Phenol, diethylketone, and alkaline earth metal (Mg, Ca, Sr, and Ba) nitrate of all of reagent grade were obtained from Wako and used without further purification. A 60% hydrogen peroxide, industrial product of Kemira-UBE, was used as purchased.

A typical procedure for alkaline earth metal ion exchange treatment of H-BEA is as follows: H-BEA powder was immersed in an aqueous solution of an alkaline earth metal nitrate and heated at 358 K without stirring for more than 14 h. The amount of dissolved alkaline earth metal ion (in mol) in the aqueous solution was four times as large as that of proton (in mol) in the immersed H-BEA. After cooling to room temperature the liquid portion was removed by filtration, and the solid was washed with de-ionized water for several times, dried at 383 K, and calcined at 823 K for more than 2 h.

The oxidation reaction was carried out in a round-bottom flask equipped with a water-cooled condenser and a magnetic stirrer. Under an atmosphere of dry nitrogen the mixture of 10.00 g of phenol, 0.27 g of diethylketone and 0.20 g of zeolite in the flask were heated up to 373 K using an oil bath. At the reaction temperature 0.10 g of 60% hydrogen peroxide aqueous solution was added using a syringe into the reaction mixture to start the reaction. The same amount of hydrogen peroxide aqueous solution was added at 1.5 and 3.0 min, so that the total amount of hydrogen peroxide added to the reaction mixture was 0.3 g. The reaction temperature was maintained for 5 min, and then cooled to room temperature. The catalyst was removed by filtration and the liquid portion was analyzed by using a Shimadzu GC-2010AF gas chromatograph equipped with a 30 m capillary column of TC-17 and an FID detector.

Diffuse-reflectance FT-IR (DR-FTIR) spectra were recorded on a Perkin-Elmer Spectrum One, equipped with an MCT detector and a Spectratech gas tight diffuse-reflectance unit. An amount of 8–15 mg of samples were put in the sample holder in the diffuse-reflectance unit. All samples were thermally treated at 823 K under a dry nitrogen flow for 2 h in the sample holder prior to observation. In the case of observation of adsorbed pyridine, small amount of liquid pyridine, typically 0.2 μl × 5 μl, was added into the nitrogen flow through the injection port heated to ∼373 K and adsorbed on samples heated to 423 K. In order to observe the pyridine desorption behavior, the sample with adsorbed pyridine was stepwise heated to 523, 623, 723, and 823 K under a nitrogen flow, respectively. The sample temperature was hold at these temperatures for 45 min, and cooled to 423 K. All spectra were recorded at 423 K.

NH_3-TPD spectra of H-BEA and alkaline earth metal ion exchanged H-BEA were recorded on an Ohkura Riken TPD instrument at Idemitsu Techno Research Center. NH_3 gas was adsorbed for 15 min and evacuated for 5 min at 373 K. Then the temperature was raised at the rate of 20 K/min under He flow.

3. Results and discussion

3.1. Diffuse-reflectance FT-IR study of OH groups on H-BEA and AE/H-BEA

Fig. 1 shows the DR-FTIR spectra in the region of OH group stretching mode on H-BEA and Ca/H-BEA. The absorption peaks at 3604 and 3741 cm^{-1} observed on both H-BEA and Ca/H-BEA have been assigned to Si–(OH)–Al bridge structure and lone silanol Si–OH, respectively [2–5] (Table 1).

The absorption peak at 3782 cm^{-1} was assigned to an external Al species in a transition structure in which, for example, the external Al species is present at a defect of BEA zeolite framework [2–5]. This peak intensity was affected by ion exchange treatment with monovalent alkaline metals such as Na [3], and with divalent metals such as Co [4]. Bortnovsky et al. suggested that the divalence ion of Co was introduced into H-BEA (Si/Al = 12.7) at a site where two framework Al atoms are near each other [4].

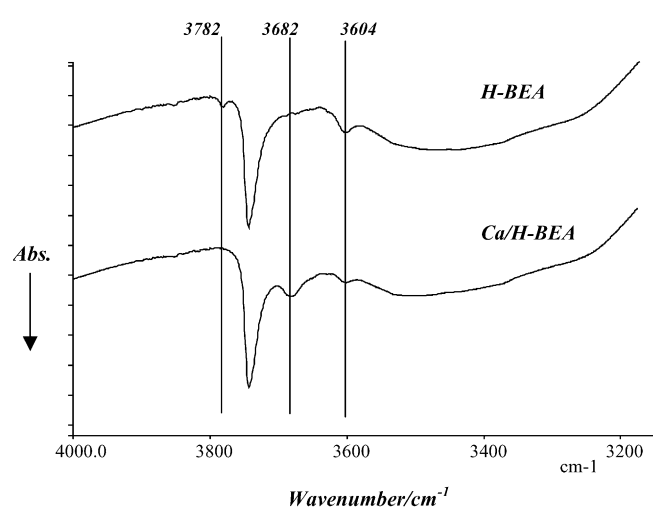

Fig. 1. DR-FTIR spectra of the hydroxyl region of H-BEA and Ca/H-BEA. The spectra were recorded under N_2 flow at 423 K. Vertical line indicates absorbance.

Table 1
Wavenumber (cm^{-1}) of absorption peaks in DR-FTIR spectra in the OH stretching region of H-BEA and Ca/H-BEA

	Al—OH—Si	OH-AE	Si—OH	OH
H-BEA	3604		3742	3780
Mg/H-BEA	3604	3692	3742	
Ca/H-BEA	3604	3682	3742	
Sr/H-BEA	3604	3679	3742	
Ba/H-BEA	3604	3672	3742	

OH-AE: absorption peak depending on alkaline earth metals; OH: OH group strongly interacting with pyridine.

The absorption peak at 3782 cm^{-1} disappeared after the Ca ion exchange treatment, while a new absorption peak at 3682 cm^{-1} appeared on Ca/H-BEA. The wavenumbers of the peaks in the region of OH group stretching vibration on ion exchanged H-BEA are given in Table 2. The peak at 3782 cm^{-1} was not observed on any of these AE/H-BEAs. The position of peaks at around 3680 cm^{-1} on AE/H-BEAs depends on the kind of alkaline earth metal, and the wavenumber increased with decreasing radius of the alkaline ion. This suggests that the peak at around 3680 cm^{-1} should be assigned to the structure in which the introduced ion interacts with OH group, or the structure such as AE-OH.

Now, we are trying to depict a probable local structure for the room of divalence ion in BEA framework by means of both computational and spectroscopic methods [6].

3.2. Acidic property of OH groups on H-BEA and AE/H-BEA measured by pyridine adsorption method

Fig. 2 shows the DR-FTIR difference spectra of pyridine adsorbed on H-BEA. It is revealed that the peaks at 3782 and 3604 cm^{-1} observed on H-BEA interacted with the adsorbed pyridine. The difference peak at 3604 cm^{-1} decreased with raising temperature. This indicates that the adsorbed pyridine desorbed at higher temperature.

In contrast, the decrease in the difference peak at 3782 cm^{-1} was not observed even at the temperature as high as 823 K. This phenomenon can be rationalized by assuming that the OH group showing the peak at 3782 cm^{-1} is a very strong acid and that the adsorbed pyridine on this OH group hardly desorbs even at 823 K. Unfortunately, the exact structure of this OH group has remained unclear.

Table 2
Phenol oxidation over H-BEA and AE/H-BEA

Catalyst	H_2O_2 base			
	CL yield (%)	HQ yield (%)	CL + HQ yield (%)	CL + HQ select. (%)
H-BEA	51.4	33.6	85.0	86.3
Mg/H-BEA	54.0	39.3	93.3	94.6
Ca/H-BEA	55.6	40.5	96.1	97.6
Sr/H-BEA	53.6	40.4	94.0	95.3
Ba/H-BEA	54.0	40.0	94.0	95.3

Cat: 0.20 g; PhOH: 10.00 g; diethylketone: 0.27 g; 60%H_2O_2aq: 0.30 g; reaction temperature: 373 K; reaction time: 5 min.

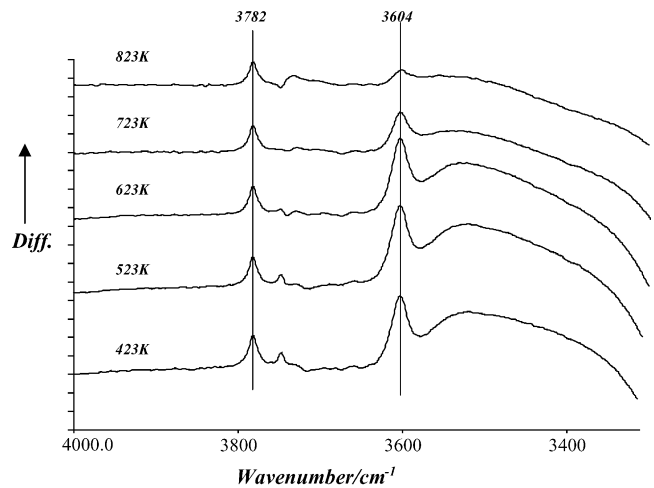

Fig. 2. DR-FTIR difference spectra between pyridine adsorbed and bare H-BEA. Difference spectra are shown as difference in absorption intensity between spectrum of bare H-BEA at 423 K and that of pyridine adsorbed H-BEA at TK in arbitrary unit.

The DR-FTIR difference spectra of pyridine adsorbed Ca/H-BEA is shown in Fig. 3. Two difference peaks at 3682 cm^{-1} appeared after Ca ion exchange treatment, and 3604 cm^{-1}, which assigned to the Si–(OH)–Al structure, can be seen, indicating that both of these OH groups act as acid. The difference peak at 3682 cm^{-1} decreased in intensity at a lower temperature than that at 3604 cm^{-1}. This indicates that the OH group showing the peak at 3682 cm^{-1} has weaker acid strength than that showing the peak at 3604 cm^{-1}. Thus, it is suggested that the ion exchange treatment with Ca produced a weaker acid site than Si–(OH)–Al on H-BEA.

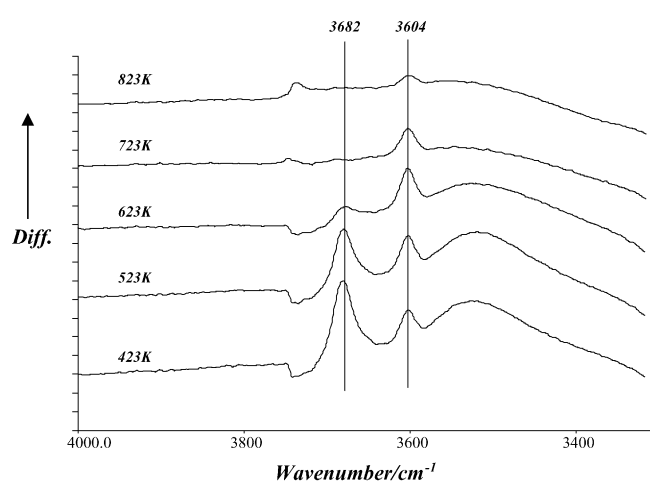

Fig. 3. DR-FTIR difference spectra between pyridine adsorbed and bare Ca/H-BEA. Difference spectra are shown as difference in absorption intensity between spectrum of bare Ca/H-BEA at 423 K and that of pyridine adsorbed Ca/H-BEA at TK in arbitrary unit.

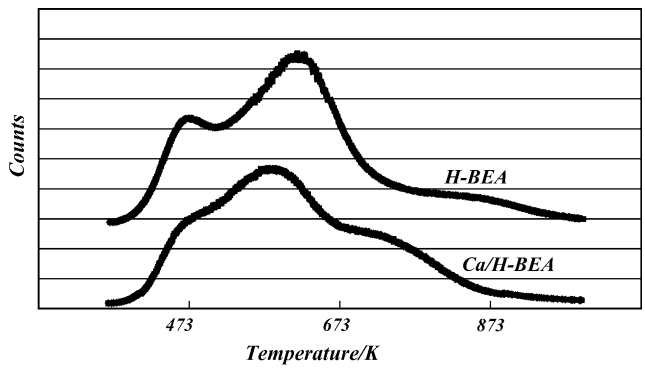

Fig. 4. NH_3-TPD profile over H-BEA and Ca/H-BEA. Heating rate = 10 K/min.

3.3. Acid property of H-BEA and Ca/H-BEA measured by NH_3-TPD method

NH_3-TPD profiles on H-BEA and Ca/H-BEA are shown in Fig. 4. It is indicated that the strong acid site on H-BEA showing desorption peak at around 873 K disappeared by the Ca ion exchange treatment. The peak has been assigned to NH_3 desorbed from very strong acid site [7]. This observation indicates that the very strong acid site was removed by the ion exchange treatment with Ca. Also, as can be seen in Fig. 4, the peak at around 623 K broadened and/or shifted to lower temperature.

The peak at around 623 K has been assigned to NH_3 desorbed from Si–(OH)–Al. The broadening and/or shift to lower temperature of this peak suggest that the amount of Si–(OH)–Al site decreased, or new acid site weaker than Si–(OH)–Al appeared, by the ion exchange treatment with Ca. From the comparison with Fig. 3, though the peaks of NH_3 desorption from Lewis and Bronsted acid are indistinguishable, it can be said that a portion of the shoulder region lower than 623 K is corresponding to the OH group showing the peak at 3682 cm^{-1}, which is weaker than Si–(OH)–Al.

On the other hand, a new peak at around 743 K was observed after the ion exchange treatment with Ca. This indicates the appearance of a new acid site stronger than Si–(OH)–Al. The DR-FTIR study of Ca/H-BEA showed no Bronsted acid site stronger than Si–(OH)–Al. Therefore, this new stronger acid site could be of the Lewis acid type.

3.4. Phenol oxidation over H-BEA and AE/H-BEA

As mentioned above, the ion exchange treatment affects the acid property of H-BEA. Both the weaker acid, which shows a DR-FTIR peak at 3682 cm^{-1}, and the stronger acid, which shows an NH_3-TPD peak at around 743 K, appeared after the ion exchange treatment. In addition, the very strong acid site, which shows an NH_3-TPD peak at around 873 K, was removed by this treatment. In this section, we will discuss the effect of the ion exchange treatment on the catalytic performance of H-BEA for the phenol oxidation.

As we reported in the previous paper [1], inorganic acids such as sulfuric acid act as catalysts in the oxidation of phenol. We also found out that some zeolites such as BEA, FAU, MOR, and MFI types in the proton form act as catalysts, and among of these, BEA in the proton form, H-BEA, shows the highest activity. The prominent feature of H-BEA was that only few tar accumulated after the reaction. The tar formation has been considered to be caused by strong acid sites [1]. We inferred from these results that both the large pore structure and the moderate acid strength of BEA are the cause of its high activity. We further investigated the improvement of the reaction yield by controlling the acid property of BEA.

Table 2 shows the results of the phenol oxidation with hydrogen peroxide over H-BEA and AE/H-BEA in the presence of diethylketone. The selectivity for diphenols, catechol and hydroquinone, based on the added hydrogen peroxide, improved by the ion exchange treatment with each alkaline earth metal. Especially, the selectivity over Ca/H-BEA reached as high as 98% in 5 min. We consider that the diethylketone is one of the key components in this catalytic oxidation system. The role of diethylketone was discussed in our previous paper briefly [1], and about this, we are investigating continuously.

In the case of Ca/H-BEA, very smaller amount of tar accumulated in the reaction mixture than in the case of H-BEA. Since tar production is expected to occur on a strong acid site, the removal of the strong acid site by the ion exchange would be the main reason for the improvement of the selectivity [1].

4. Conclusion

We investigated the effect of the ion exchange with alkaline earth metal such as Ca on the catalytic performance of H-BEA in the phenol oxidation. The ion exchange treatment modified the acid property of H-BEA, and also improved the selectivity of the oxidation of phenol. On the basis of these results, we expect that a very selective, thus green, catalytic oxidation system will be able to be constituted with solid acid such as zeolite having precisely controlled acid property. Unfortunately, we could not make it clear what type of acid site on Ca/H-BEA is catalytically active for the phenol oxidation. Also, it has remained unclear whether the introduced alkaline earth metal itself works as a catalytically active site or not. Furthermore, the role of diethylketone over AE/H-BEA has not been clarified. These points will be discussed continuously elsewhere.

Acknowledgement

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