Acid and Base Properties of Chemical-Treated Natural Zeolite

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Abstract   To study the acid and base properties of chemical-treated natural zeolite, FT-IR analysis was performed by the adsorption of pyridine and pyrrole and thermo-gravimetric analysis was done by the adsorption of NH_3. These solid catalysts have two acid sites, which are related to the Brönsted and Lewis acid sites, respectively. HCl-treatment led to the increased acidity and the maintained basicity. Acidity of NaOH-treatment samples also increased with the NaOH-treatment but basicity decreased. The p-xylene selectivity on the chemical-treatment zeolite was higher than that on the untreated zeolite.

1. Introduction

Zeolite catalysts are characterized by the ratio of Si/Al, uniform intracrystalline cavities and pores, the species of cations in these cavities, adsorption property and acid sites[1~4]. Since zeolite X was used as a cracking catalyst in petroleum industry, these catalysts have been used in reforming of naphthas, methanol to gasoline(MTG) process, olefins synthesis, ethylbenzene synthesis, xylene isomerization, etc.[5,6].

In recent years, the demand for p-xylene has increased because its derivatives were applied in new and expanded area. But the synthetic xylene contained three types of isomers in the equilibrated mixture. After the seperation of p-xylene from this mixture, the isomerization of o- and m-xylene to p-xylene was needed[1,7].

In the past, the isomerization of xylene was performed on the acid catalysts such as Friedel-Crafts and silica-alumina, but these catalysts had shown the low selectivity and the severe deactivation[5,9]. After the development of zeolite with good selectivity and activity in 1970s, many researchers have studied the synthesis and isomerization of xylene on this catalyst[10,11].

It has been well known that the isomerization mechanisms of xylene on zeolite are intramolecular 1, 2-methyl shift mechanism and intermolecular transalkylation mechanism and these are closely related to the acidity of zeolite[12].

In this study, the acidity and the basicity of natural zeolite treated with various concentration of HCl and NaOH were investigated by FT-IR and thermo-gravimetric analyses. And the isomerization of xylene on these catalysts was also studied.

2. Experiment

2-1. Preparation of zeolite sample

Natural zeolite from Kampo area was treated with various concentration of HCl and NaOH solution at 100℃ for 2hr[4,13].

2-2. Analysis of acidity and basicity

Acid and base properties of zeolite samples were analyzed by FT-IR in the range of 400-4000cm^{-1} and thermo-gravimetry.

80mg of zeolite : KBr=1 : 25 was compressed at 8ton/cm^2 and activated at 500℃ for 5hr. Adsorption was carried out by probe molecules for 30min at room temperature and desorbed for 1hr at 100℃ or 200℃. The probe molecule for acidity analysis was pyridine and

① N₂ Cylinder ② Dehumidifier ③ Flow Meter ④ Microfeeder
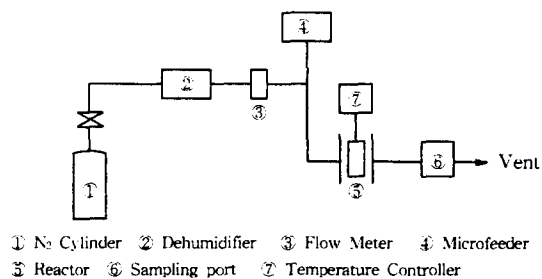⑤ Reactor ⑥ Sampling port ⑦ Temperature Controller
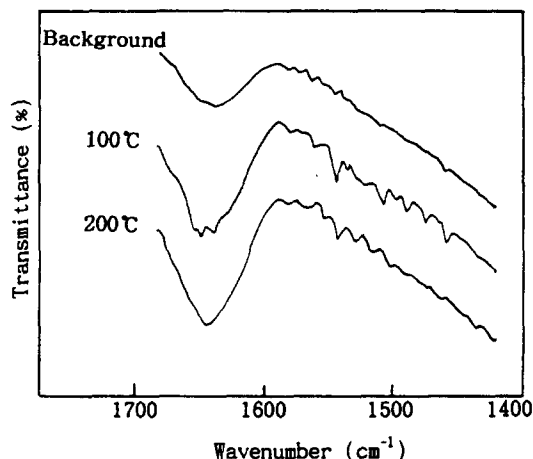
Fig. 1 Schematic diagram of experimental apparatus.

Fig. 2. FT-IR spectra of pyridine adsorbed on untreated natural zeolite after evacuation at different temperatures for 1hr.
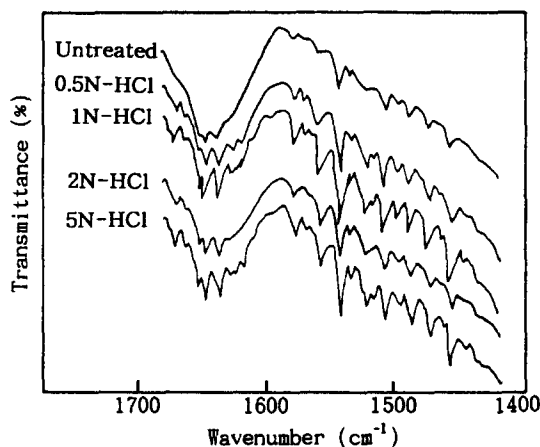

Fig. 3. FT-IR spectra of pyridine adsorbed on HCl-treated zeolite after evacuation of 100℃ for 1hr.

that for basicity analysis was pyrrole.

Thermo-gravimetric analysis was carried out as follows. To remove water from intracrystalline cavities of zeolite samples, these were placed in furnace of 500℃ for 5hr and were adsorbed by NH₃ for 1hr. The loss of NH₃ by heat was analyzed by thermo-gravimetry.

2-3. Isomerization of o-xylene

The apparatus for isomerization of o-xylene was shown in Fig. 1. Zeolite(1mg) was placed in copper tube and activated at 400℃ for 2hr at the nitrogen atmosphere with the flow rate of 10ml/min. Under these conditions, 1ml/min of o-xylene was fed by microfeeder and the product was analyzed by gas chromatography.

3. Results and Discussion

The natural zeolite used in this study was found out as clinoptilolite type by x-ray diffraction[4]. To analyze the acid property of the untreated natural zeolite, FT-IR analysis was performed and the spectra were shown in Fig. 2. The natural zeolite showed two acid siteswhich were related to the Brönsted(1540 cm⁻¹) and Lewis(1445cm⁻¹) acid sites. Brönsted acid site was strong which acted as a proton donor and Lewis acid site was weak which acted as an electron pair acceptor. With the increase of desorption temperature, the intensities of these two acid sities decreased and Lewis acid site disappeared at 200℃ while Brönsted acid site decreased slightly. From this result, it could be confirmed that Brönsted acid site was more stronger than Lewis acid site.

Fig. 3 showed the acid property on zeolite at various HCl-treat concentration. All samples also had two acid sites and the intensities of them were in increment with the increase of HCl-treatment concentration. As aluminum was extracted from the crystal lattice by the attack of HCl, the concentration of acid site was lowered but the intensity of the rest sites became strong. This was confirmed by the thermo-gravimetric analysis as shown in Fig. 4. The amount of NH₃ desorbed was propor-
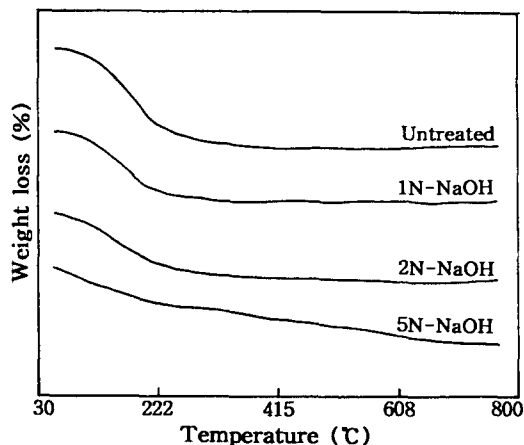
Fig. 4. Thermo-gravimetric curve for HCl-treated zeolite after adsorption of NH₃

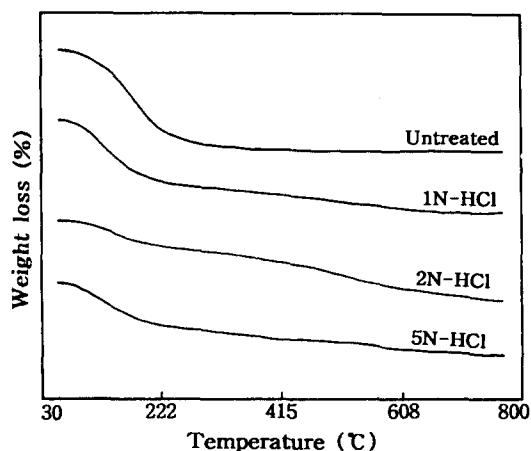
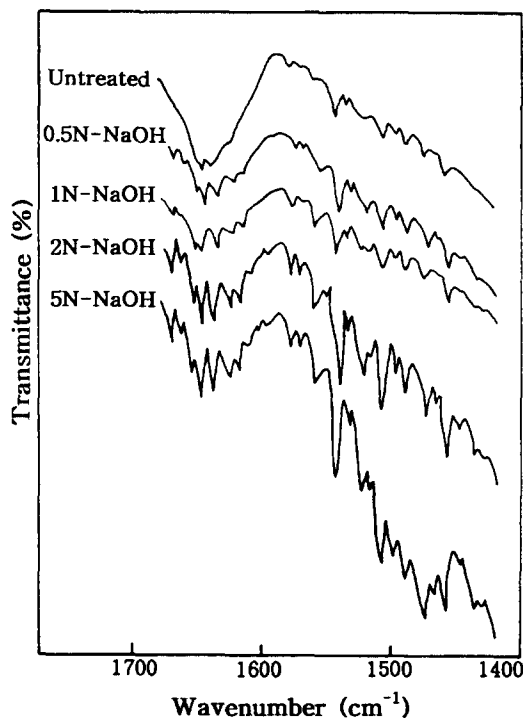Fig. 6. Thermo-gravimetric curve for NaOH-treated zeolite after adsorption of NH₃

Fig. 5. FT-IR spectra of pyridine adsorbed on NaOH-treated zeolite after evacuation at 100℃ for 1hr.

higher point. This meaned that NH₃ physisorbed weakly on the Lewis acid site was desorbed at low temperature but NH₃ chemisorbed strongly on the Brönsted acid site needed more energy to desorb.

Fig. 5 showed the acid property on various NaOH-treated zeolites. Like the HCl-treated zeolite, two acid sites appeared and the intensities increased with the increase of NaOH concentration. Aluminum can also be extracted by the attack of NaOH in this case. Hence, as explained in Fig. 4, the amount of acid site decreased but the intensity increased with the increase of Si/Al ratio.

To investigate the base property of zeolite sample, FT-IR analysis was carried out for the samples adsorbed with pyrrole and the spectra were shown in Fig. 7. The peaks of NH-combination band in pyrrole were appeared at 2940 cm⁻¹ and 2850cm⁻¹ and these bands decreased slightly with the chemical treatment. It's well known that strong basicity exert a bad influence for the isomerization of xylene.

The products of o-xylene isomerization on these zeolite catalysts were listed in Table 1. It is well known that isomerization of xylene isrelated to the concentration and strength of acid sites. Two well established mechanisms of

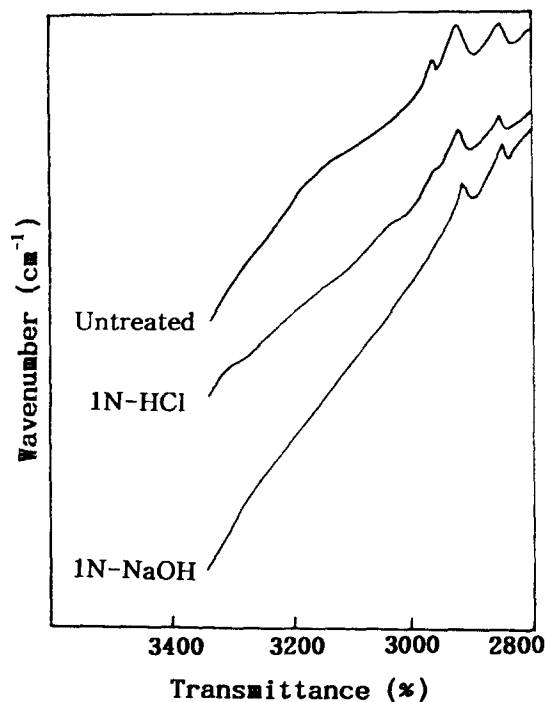tional to the distribution and intensity of acid sites. The total amount of of NH₃ desorbed decreased with the increase of HCl treatment concentration. With the increment of HCl treatment concentration, however, the desorption temperature of NH₃ appeared at

Fig. 7. FT–IR spectra of chemical–treated zeolite adsorbed with pyrrole after desorption at 100℃ for 1hr.

xylene isomerization are intramolecular 1,2–methyl shift (mechanism 1) and intermolecular transalkylation (mechanism 2). The former needs one adsorption site but the latter needs two adjacent adsorption sites. In the products of Table 1, xylene isomers were produced through the mechanism 1 and amount of xylene isomers was o–xylene>m–xylene>p–xylene because o–xylene was a reactant and the path was o–xylene⇌m–xylene⇌p–xylene. So, much m–xylene can be produced than p–xylene statistically. The ratio of toluene and trimethylbenzene was about 1 : 1 for all zeolite samples because these products were from mechanism 2. On the comparison of product amounts from mechanisms 1 and 2, those from mechanism 1 was larger than those from mechanism 2.

As natural zeolite was treated with HCl and NaOH, the conversion of o–xylene decreased and the selectivity of p–xylene increased. The decrement of o–xylene conversion can be explained by the decrement of concentration of

Table 1. Products Distribution from Isomerization of o–Xylene on Chemical–treated Natural Zeolite for 1hr.

Sample	p–xylene	m–xylene	o–xylene	Toluene	TMB[a]	Conversion (%)	Selectivity of p–xylene
Untreated	14.5	29.3	49.1	2.8	3.0	50.9	28.5
1N HCl	12.7	16.3	64.7	2.8	2.9	35.3	36.0
2N HCl	11.5	14.2	67.1	2.6	2.8	32.9	35.0
5N HCl	10.9	12.1	70.4	3.1	3.0	29.6	36.8
1N NaOH	11.5	14.6	64.3	2.8	2.9	35.7	32.2
2N NaOH	10.1	12.5	70.6	2.5	2.5	29.4	34.3
5n NaOH	9.6	10.3	73.5	3.1	3.0	26.5	36.2

a : Trimethylbenzene

acid site. With the proceeding of o–xylene conversion, coke was deposited in the pore of zeolite so that the diffusion of components was disturbed. So, the selectivity of p–xylene, which can easily diffuse out from the pore of zeolite in comparison with o– and m–xylene, increases.

4. Conclusions

From these results, the following conclusions could be drawn.
1. All these zeolite catalysts showed two acid sites, Brönsted (1540cm⁻¹) and Lewis (1445 cm⁻¹) acid sites.

2. The acid intensity of zeolite increased and the acid site distribution of that was lowered with the increase of chemical-treatment concentration. And the basicity is lowered slightly.

3. With the treatment of natural zeolite by HCl and NaOH, the conversion of o-xylene decreases and the selectivity of p-xylene increases.

Acknowledgement

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