

九龍浦產 天然제올라이트의 物性 및 觸媒特性

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The Physical and Catalytic Properties of Kuryongpo Natural Zeolite

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요 약. 경북 구룡포산 천연제올라이트에 대한 물리적 성질과 촉매활성이 검토되었다. 정량분석과 X선 회절스펙트럼으로부터 천연제올라이트는 30~40%의 mordenite를 함유하고 있다. 원시료의 표면적은 $75 \text{ m}^2/\text{g}$ 에 불과하나 2N 염산으로 처리시 $320 \text{ m}^2/\text{g}$ 에 이른다. 톨루엔불균화 반응에 대해서도 2N에서 최대의 전화율을 보여주나, 활성저하가 심한 것으로 나타났으며 크실렌에 대한 벤젠의 선택성은 처리한 산농도가 증가함에 따라 감소하는 것으로 나타났다.

ABSTRACT. The properties of the natural zeolite produced in Kuryongpo, Kyung-sang-Bukdo, were investigated by X-ray diffraction analysis, chemical composition analysis, and nitrogen adsorption experiment. The quality of the acid treated natural zeolite as the catalyst for the disproportionation reaction of toluene was examined experimentally by observing the conversion in a microcatalytic reactor.

The quantitative analysis and X-ray diffraction spectrum showed that the zeolite ore of Kuryongpo contained approximately 30 to 40 per cent of mordenite structure. The surface area of the zeolite ore was $75 \text{ m}^2/\text{gm}$ and increased to a maximum value of $320 \text{ m}^2/\text{gm}$ after treatment with 2N HCl solution. The catalytic activity for the toluene disproportionation reaction was maximum when the zeolite treated with 2N HCl solution was used. The selectivity of xylene to benzene decreased with increasing degree of acid treatment.

INTRODUCTION

Mordenite is a zeolite which is either mined in nature or can be synthesized. Because of its high silica-alumina ratio, it has high thermal

and acid stabilities. Because of its high acid stability, mordenite can be treated with acid directly for decationization and enhancement of the silica-alumina ratio. The effective pore dia-

meter of natural mordenite can be increased to adsorb large molecules like benzene when they are changed into H-form by the acid treatment.² It is possible to increase the silica-alumina ratio of natural mordenite to 100 without affecting the crystalline structure.¹ Natural mordenite is used for nitrogen removal in carbon dioxide, the removal of ammonium ion and Cd^{2+} ion in waste water and radioactive waste. One-dimensional pore structure makes the large port mordenite applicable to xylene separation and toluene disproportionation.

In Korea, natural zeolites are found in Youngil Bay Area, and the adsorption and catalyst characteristics of the acid-treated clinoptilolite found in Yangbuk-myun area has been studied by Chon.³ The natural zeolite found in Kuryongpo, Kyung-sang-Bukdo has a partial mordenite structure. In the present study, the physical and catalytic properties of Kuryongpo zeolite are investigated by X-ray and chemical analyses, adsorption experiments and toluene disproportionation reaction experiments.

EXPERIMENTAL

The original sample was prepared by crushing the yellowish-white, cleavable, plate-shaped natural zeolite ore, which was mined in Kuryongpo, Kyung-sang-Bukdo, to 100 mesh size.

30 grams of 100 mesh original sample and 450 ml HCl solution were introduced to 1 liter flask with reflux condenser and boiled at 100°C for four hours with mechanical stirring. The sample was then washed and filtered with distilled water until Cl^- ions were not detected with AgNO_3 solution, and then dried for one day at 150°C.

The crystalline structure was studied by observing the X-ray diffraction spectrum obtained by Norelco spectrometer with $\text{CuK}\alpha$, 35 KV,

15 mA, a time constant of 2 and a scanning speed of 4 deg/min. The chemical analyses were carried out by the gravimetric analysis for SiO_2 and the ignition loss, by the dichromate method for iron compounds, by EDTA titration for aluminum and by atomic absorption spectrometry for other components.

The amount of nitrogen adsorbed was measured by conventional volumetric system at liquid nitrogen temperature. The sample was dehydrated to 10^{-4} mmHg by heating at 200°C for two hours, and nitrogen was purified by passing it through a Linde 4 A molecular sieve bed at liquid nitrogen temperature.

Adsorption of benzene was studied at room temperature and the amount of benzene adsorbed was taken at 30 mmHg.

The schematic diagram of the microreactor system for the toluene disproportionation reaction is shown in Fig. 1. Nitrogen was saturated with toluene in the saturator surrounded in the air bath at 30°C before being fed to the reactor. The products were sampled by the sampling device consisting of two 6-port, a 3-port and a gate valve. The reactions were carried

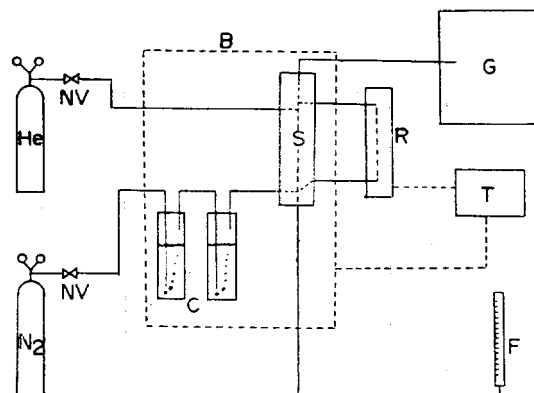


Fig. 1. Schematic diagram of the microreactor system. B, Convective air bath; C, Toluene saturator; F, Bubble flow meter; G, Gas chromatograph; NV, Needle Valve; R, Reactor & heater; S, Sampling device (Valve & Ports); T, Proportional temperature controller.

out either continuously or pulse by suitable connections of ports and valve of the sampling device. The nitrogen flow rate was 30 ml/min. 0.3 gram of cylindrical catalyst pellets ($4.4 \times 1.6 \phi$ mm) was packed in the central part of the reactor and activated by helium (30 ml/min) at 550 °C for two hours before the reaction. A varian 1420 gas chromatograph with a column of Benton 34+DOP (5%+5%) was used for the product composition analysis.

RESULTS AND DISCUSSION

Fig. 2 shows the X-ray diffraction diagrams

of original zeolite ore. The intensity of the diffraction line was weak and broadened compared with that of synthetic mordenite. The mordenite content was estimated to be 30 to 40 percent by comparing the peak areas with those for the synthetic mordenite.

Table 1 compares the experimental X-ray data with ASTM Card 6-0239 for natural mordenite. Other peaks show the possibility of the presence of various mixtures such as clinoptilolite, quartz.

Table 2 shows the chemical composition of the zeolite ore determined by the quantitative analysis.

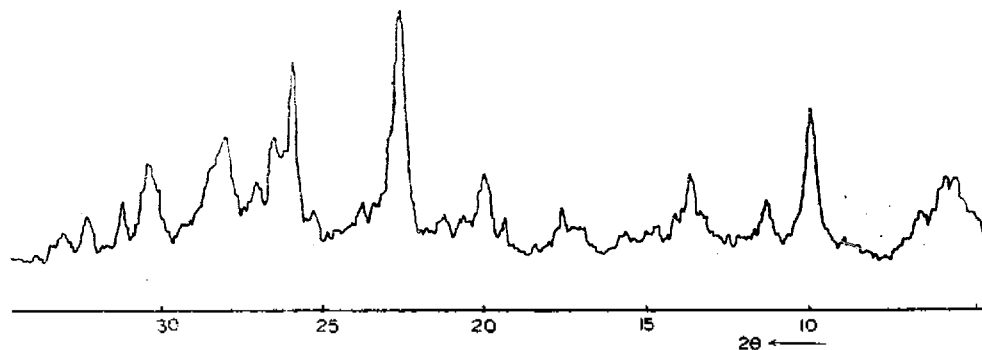


Fig. 2. X-Ray diffraction spectrum of the original zeolite sample.

Table 1. *d*-spacings of original sample and ASTM literature value.

ASTM 6-0239		Original sample		ASTM 6-0239		Original sample	
<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>d</i> (Å)	Intensity	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>d</i> (Å)	Intensity
		16.1	M	3.76	20	3.77	VW
		15.2	M	3.62	10		
13.7	50	13.6	W	3.56	10	3.55	VW
9.10	90	9.0	S	3.48	100	3.47	S
		7.9	W	3.39	90	3.40	M
6.61	90	6.6	M	3.31	10		
6.38	40	6.4	W	3.22	100	3.21	M
6.10	50	6.1	W	3.10	20		
5.79	50	5.8	W	2.946	20	2.96	M
5.03	10	5.1	W	2.896	60	2.88	W
4.87	20	4.65	VW	2.743	10	2.79	VW
4.53	80	4.58	M	2.700	30	2.73	VW
4.14	30	4.2	VW	2.639	10		
4.00	90	3.97	VS	2.560	40	2.65	VW
3.84	60			2.522	50	2.51	VW

Table 2. Chemical composition analysis of the original zeolite sample

Component	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	MgO	Fe ₂ O ₃	K ₂ O	MnO	ig. loss
Wt. %	60.97	12.81	1.96	1.05	1.09	1.83	10 ⁻¹⁻⁰	10 ⁻¹	9.25

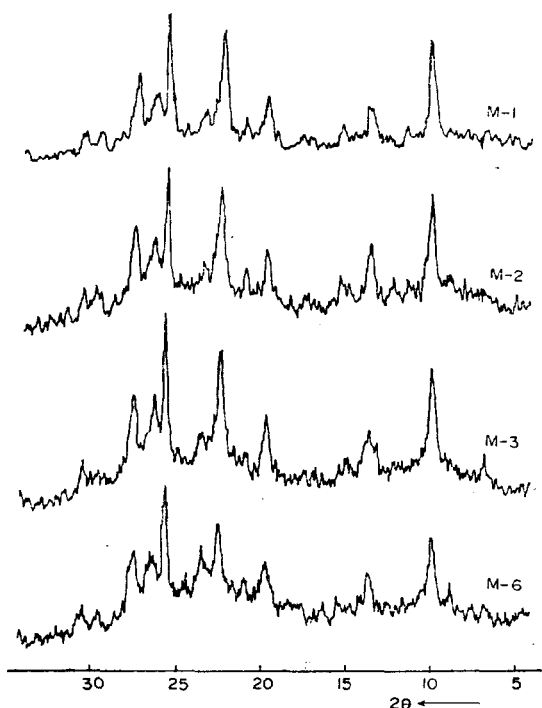
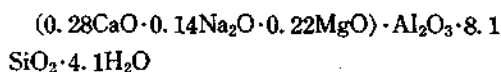
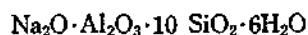


Fig. 3. X-Ray diffraction spectra of the acid-treated zeolite samples.

The oxide formular of the original sample can be written as follows:



The pure Na-mordenite has the following oxide formular⁴



having SiO₂/Al₂O mole ratio of 10.

The silica-alumina ratio of the original sample was 8.1, indicating that the mordenite content was relatively small and clay mixtures were present in the sample. The clay mixtures were shown to be mostly amorphous by X-ray analysis.

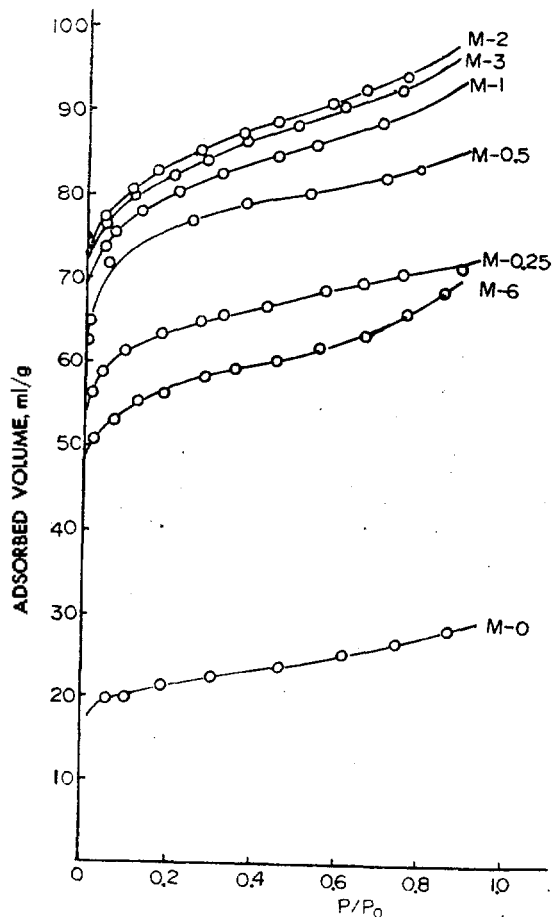


Fig. 4. Adsorption isotherms of nitrogen for original and acid-treated samples.

The adsorption isotherms shown in Fig. 4 are combinations of type I and type II as classified by Brunauer,⁵ type II characteristics becoming more pronounced with increasing degree of acid treatment indicating that pores became enlarged with the acid treatment.

Fig. 5 shows adsorbed volume of nitrogen and surface area obtained by BET equation. The surface area of the original sample was 75 m²/g and increased to a maximum value of 320

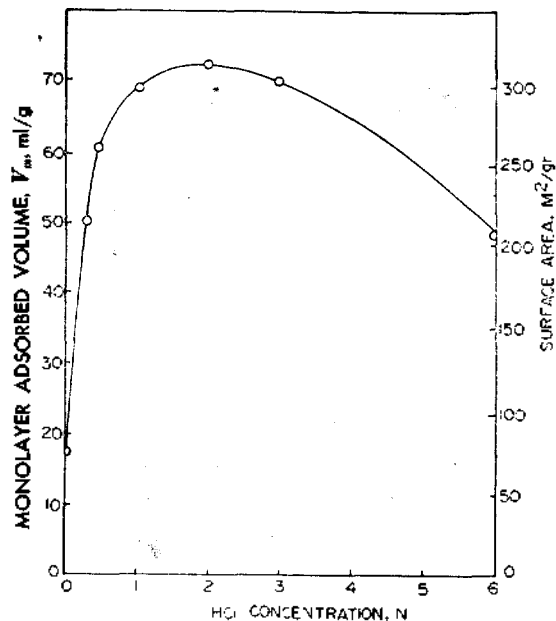


Fig. 5. Monolayer adsorbed volume and surface area of the original and acid-treated samples.

m^2/gm when the sample was treated with 2 *N* HCl solution. Two factors may cause the increase in the adsorbed volume with acid treatment. One is a proportional factor due to enlargement of pore size by decationization, extraction of impurities, and rearrangement of the structure by the removal of aluminum and impurities. The other is an inversely proportional factor due to the decrease in micropores as the structure of the acid-treated sample collapsed. The increasing tendency of adsorbed volume was observed until micropores did not suffer noticeable deformation.

Fig. 6 shows the effect of acid treatment on the catalytic activity in the pulse microreactor for toluene disproportionation reaction. The conversion of toluene and the deactivation rate were maximum when the acid concentrations for catalyst treatment were 2 *N* and 1 *N* respectively. The experimental result that acid treatment [increased the conversion indicated that acid treatment enlarges the pore size of the ori-

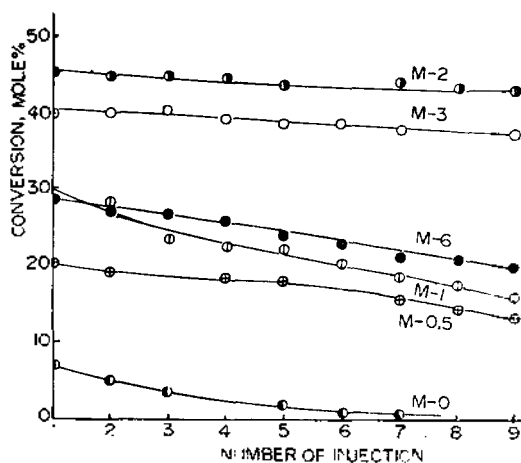


Fig. 6. Catalytic activity of the original and acid-treated zeolite with number of injection.

ginal sample.

The amount benzene adsorbed increased from 3.6 cc/g for original sample to 10 cc/g for the sample treated with 1 *N* HCl. Thus the pore size of the catalyst becomes large enough for reactant and products to diffuse freely.

The catalyst treated with 6 *N* shows a decrease in conversion due to the decrease in conversion. This may be due to collapse of pore structure as evidenced from the decrease in nitrogen adsorption and in peak intensities of X-ray powder diagrams.

Fig. 7 shows the conversion and selectivity as functions of the acid concentrations in the continuous microreactor system. The catalyst deactivation was very fast, indicating that the coke formation was very severe when the reaction was carried out with nitrogen gas instead of hydrogen.⁶ Hydrogen probably promote the hydrogenation of some reaction products whose deposition on the catalyst would cause its deactivation.

Both disproportionation and dealkylation reactions of toluene can take place. The fact that xylene to benzene ratio was around 1, indicates that disproportionation reaction was the domin-

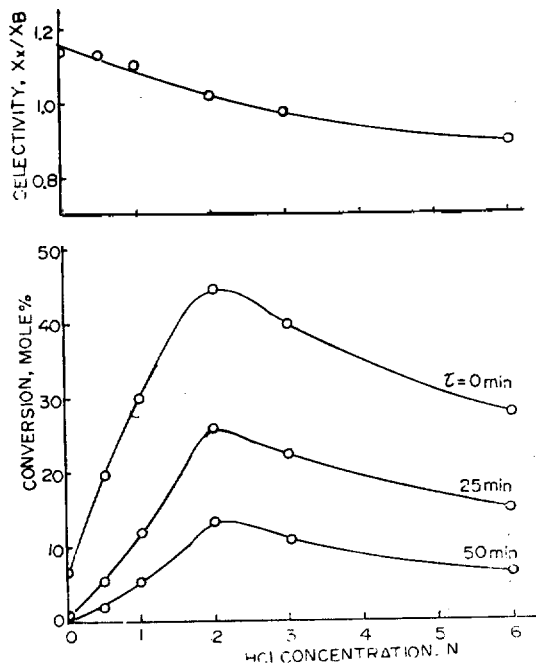


Fig. 7. Selectivity and conversion vs. acid concentration. τ , Reaction time; Reaction temp., 550 °C.

ant reaction. Not obvious was the reason for the xylene/benzene to be over 1 for samples treated with less than 1 N HCl. Xylene/benzene showed the decrease with increasing degree of acid treatment. It may be that with the increasing degree of acid treatment the concentration of active sites which favor the dealkylation reaction increased.

CONCLUSIONS

1. The natural zeolite produced in Kuryongpo

contained 30 to 40 per cent of the mordenite structure.

2. The rearrangement of pore structure and pore size enlargement effects by decationization and extraction of aluminum and other impurities increased the surface area of the original sample from 75 m²/g to a maximum value of 320 m²/g when the sample was treated with 2 N HCl solution.

3. The conversion for toluene disproportionation reaction in the microreactor was maximum when the natural zeolite treated with 2 N HCl solution was used. High deactivation tendency was observed near 1 N acid concentration because of severe coke deposition on the catalyst surface by strong acid sites.

4. The selectivity of xylene to benzene decreased with increasing degree of acid treatment.

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