

Liquid-Phase Degradation of HDPE over Alkali-Treated Natural Zeolite Catalysts

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Abstract—Catalytic performance of alkali-treated natural zeolites was studied in the liquid-phase catalytic degradation of HDPE. Alkali treatment of natural zeolite with a moderate NaOH solution brought about the formation of mesopores and a decrease in acid site density, resulting in a considerable improvement of its catalytic activity. However, alkali treatment with highly concentrated NaOH solutions induced zeolite structure destruction, resulting in lower activity. HDPE conversion and product selectivity of alkali-treated natural zeolites were discussed in terms of their pore structures, acidities and the diffusion properties of large molecules.

Key words: HDPE, Natural Zeolite, Degradation, Alkali Treatment

INTRODUCTION

Polymer production has steadily increased due to its convenience, excellent processibility, and low price. With the rapid increase of waste polymers, however, efficient and ecologically safe ways of disposing the waste have not as yet been established. Although burying and incineration are convenient, they cause severe soil contamination and air pollution. The conversion of waste polymers to fuels or chemical feedstocks is an effective way of recycling and reducing pollution, but it is prohibitively expensive.

The liquid-phase degradation of polymeric materials over MFI and BEA zeolite catalysts produces high quality fuels with good yields, even at low temperatures [Hwang et al., 1998; Manos et al., 2000; Puente and Sedran, 1998; Shim et al., 1998; Walendziewski and Steczyslaw, 2001; You et al., 2000, 2001]. The formation of high-boiling hydrocarbons -- which deposit on the catalyst surface, resulting severe deactivation - was suppressed due to their bent-type pores. Nevertheless, the high cost of synthetic zeolites, prepared by hydrothermal reaction from the synthesizing gel, containing expensive organic templates, reduces the economic merit of catalytic degradation. The low price of the liquid fuel obtained, compared to the high cost of synthetic zeolites, makes it difficult to commercialize the liquid-phase catalytic degradation, as a cost-effective recycling process.

The price of natural zeolites is very cheap compared to that of synthetic zeolites [Lee et al., 1999], but their catalytic activities are extremely low. The low activity is primarily the consequence of the small pores and improper acidities of natural zeolites. In addition, impurities covered on the surface and clogged the pores of the natural zeolite mask active sites, reducing its catalytic activity. The low content of zeolite phase in natural zeolites also lead to their low activities.

The removal of impurities from natural zeolites by acid treatment, accompanied by an increase in zeolite contents, may be helpful in enhancing their catalytic activities [Jeong et al., 2001]. A partial

breakage of pore entrances by the dissolution of aluminum, enhances the diffusion rate of the large polymer molecules. In addition, a decrease in the number of aluminum atoms in zeolite skeletons reduces their acid site densities, suppressing carbon deposits. As a result, acid treatment considerably improves the catalytic activity of natural zeolites, but it is limited in the modification of zeolite phase because of the low solubility of the silica-a major component of zeolite.

Alkali treatment, as opposed to acid treatment, has not yet been widely considered as a modification method for natural zeolites, chiefly because alkali can dissolve zeolite itself. With a proper concentration, however, it may be helpful to improve their catalytic activities, if the alkali removes only the impurities and dissolves the surface. In particular, the formation of mesopores on the zeolite surface, via partial dissolution by alkali, may improve considerably their activities by enhancing the diffusion rates of the large polymer molecules. Lowering acid site density by alkali treatment can also contribute to the suppression of carbon deposits on their external surface.

In this study, the liquid-phase catalytic degradation of HDPE was carried out over alkali-treated natural zeolite catalysts. The variation of their catalytic activities by varying the extent of the alkali treatment was discussed relating to the changes in the pore structures and acidic properties of the natural zeolites.

EXPERIMENTAL

1. Preparation and Characterization of Natural Zeolite Catalysts

Natural zeolite, provided by Handoo Co., was used as a starting material. Particles within 75-45 μm diameter were sieved. The natural zeolite was treated with an alkali solution in a round-bottom flask equipped with a condenser at 60 °C for 5 h.

The concentration of NaOH solution was varied from 1.0 N to 8.0 N. After the alkali treatment, the natural zeolites were refluxed with 0.5 N HCl solution at 60 °C to exchange their cations with protons. Carefully washed proton-form natural zeolites were then dried at 100 °C overnight. The alkali-treated natural zeolites are denoted as BNZ(x) by designating the concentration of NaOH solution in

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parentheses, while the NZ(0) catalyst represents the original natural zeolite. Synthetic mordenite (Japanese reference catalyst, JRC-Z-M-20, MOR) and clinoptilolite (CLI) [Seo et al., 1998] were used to identify the components of the natural zeolite.

X-ray diffraction patterns of the alkali-treated natural zeolites were recorded on an X-ray diffractometer (Rigaku D/MAX-1200) with a CuK α X-ray source at 40 kV and 20 mA. Changes in the surface morphology of the zeolite after alkali treatment were inspected with an SEM (JEOL, JSM-5400). Their chemical compositions were also determined using an EDX attachment (NORAN Z-Max 3000 Series) in the SEM stated above.

Nitrogen adsorption isotherms of the alkali-treated natural zeolites were obtained using a home-built volumetric adsorption apparatus at liquid-nitrogen temperature. A zeolite sample was dehydrated at 300 °C for 2 h prior to nitrogen adsorption. The adsorption rate of benzene on the alkali-treated natural zeolites was measured in a quartz-spring gravimetric adsorption system [You et al., 1999]. After evacuation at 300 °C under 1.33×10^{-4} Pa for 2 h, benzene vapor of 3.5 kPa was introduced to the zeolite samples at 20 °C. The increase in the mass of the zeolite sample was recorded for 60 min.

Temperature-programmed desorption (TPD) profiles of ammonia from the alkali-treated natural zeolites were carried out to compare their acidic properties. A zeolite sample was dehydrated in a helium flow of 150 ml·min⁻¹ at 550 °C for 2 h. Pulses of ammonia gas were introduced at 80 °C to achieve a saturated adsorption. Physically adsorbed ammonia was removed by purging the sample with helium for 1 h at the same temperature. The temperature of the reactor was increased with a ramping rate of 10 °C·min⁻¹ from 80 °C to 600 °C, and the amount of ammonia desorbed from the zeolite sample was measured using a thermal conductivity detector (TCD).

2. Liquid-phase Degradation of HDPE

The HDPE provided by Honam Petrochemical Corporation was a white granule 2-3 mm in diameter. The melting index and molecular weight of the HDPE were 0.35 and 250,000, respectively. The absorption bands attributed to C=C and C \equiv C bonds did not appear in the IR spectrum of the HDPE recorded on an FT-IR spectrophotometer (BIORAD, FTS-175C), suggesting a negligible content of non-saturated hydrocarbons. A single melting point of the HDPE was observed at 136 °C on DSC analysis, obtained using a differential scanning calorimeter (DSC; Dupont Instrument 910). The HDPE used in this study, therefore, is considered to mainly consist of saturated hydrocarbons with a comparatively narrow molecular weight distribution.

The liquid-phase degradation of the HDPE over the alkali-treated zeolite was carried out in N₂ environment using a batch reactor with a condenser (-4 °C) at 410 °C for 60 min [Shim et al., 1998]. 10 g of the HDPE and 0.5 g of a natural zeolite catalyst were charged in a 100 mL flask. Nitrogen gas removes air to prevent side reactions induced by oxygen. Gas was produced when the reaction temperature was increased to 250 °C, and liquid began to be collected in the buret from 400 °C. The amount of gas produced was measured using a wet test gas flowmeter (Ritter, TG05). The yields of gas and liquid products were defined as percentages of the produced amounts against the amount of the HDPE charged. The conversion was defined as the sum of the yields of gas and liquid products. The compositions of the gas and the liquid products were analyzed by gas chromatograph (Donnam DS-6200) with an HP-5 column (0.32

mm \times 50 m).

RESULTS AND DISCUSSION

1. Characterization of Alkali-treated Natural Zeolites

The crystalline phases of natural zeolites vary depending on their production sites. The natural zeolites produced in Korea usually contain clinoptilolite and mordenite as major components [Kang et al., 1997, 1998]. Fig. 1 compares the XRD pattern of the natural zeolite used in this study, named as NZ(0), with those of synthetic mordenite and clinoptilolite. The strong diffraction peaks of the NZ(0) zeolite were comparable to those of mordenite, rather than clinoptilolite, indicating that mordenite was the major zeolite component of the natural zeolite used in the study. Diffraction peaks of clinoptilolite were also observed on the NZ(0) zeolite, even though their intensities were very weak compared to those of mordenite. This

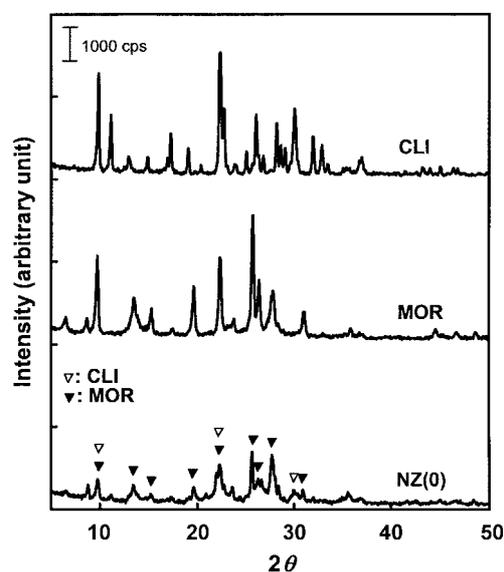


Fig. 1. XRD patterns of CLI, MOR and natural zeolites.

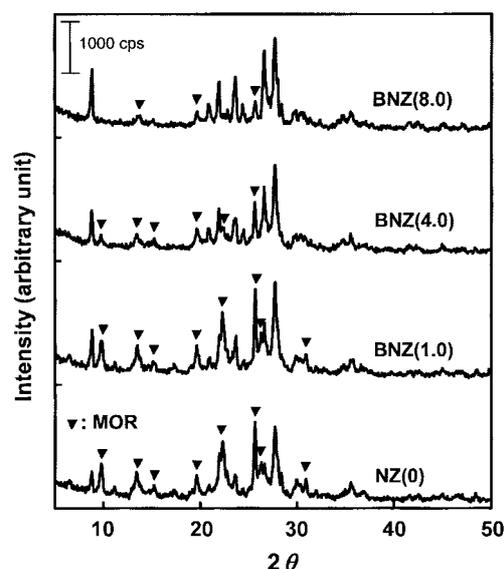


Fig. 2. XRD patterns of alkali-treated natural zeolites.

means that the natural zeolite contains a small amount of clinoptilolite as well. The content of mordenite was estimated to be about 40%.

Since zeolites are composed of silica and alumina, and alkali can dissolve the both components, alkali treatment resulted in significant changes in their components and crystalline phases, as shown in Fig. 2. Characteristic peaks assignable to mordenite were maintained with the alkali treatment of 1.0 N NaOH solution, but the characteristic peaks were substantially decreased by the alkali treatments with higher concentrations. The characteristic mordenite peaks became too small to be observed clearly on the BNZ(8.0) zeolite, indicating a significant disappearance of zeolite components with the alkali treatment using the 8.0 N NaOH solution. The remaining peaks of the BNZ(8.0) zeolite were assigned to feldspar and quartz, rendering a quite different XRD pattern from that of the original natural zeolite.

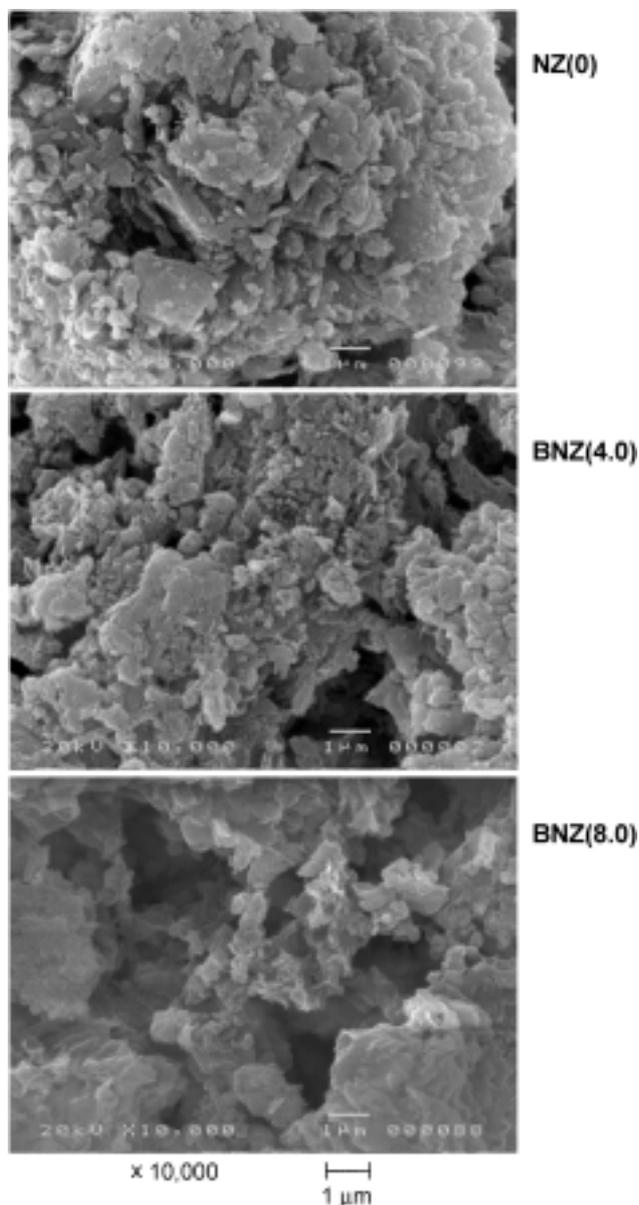


Fig. 3. SEM photos of alkali-treated natural zeolites.

Table 1. Chemical compositions of alkali-treated natural zeolites

Alkali treatment	Concentration of NaOH solution (N)				
	none	1.0	4.0	6.0	8.0
Recovery after alkali treatment (%)	-	70	55	43	40
Composition (wt%)					
SiO ₂	76.2	83.5	76.5	74.9	73.9
Al ₂ O ₃	13.1	12.0	19.1	20.0	20.6
K ₂ O	3.9	1.6	1.6	1.3	2.1
CaO	3.2	1.0	0.6	0.8	0.8
Fe ₂ O ₃	2.3	0.3	0.6	0.8	0.4
Na ₂ O	0.7	0.3	0.6	1.0	1.2
MgO	0.6	1.3	1.1	1.1	1.0
Si/Al	5.0	5.9	3.4	3.2	3.0

Dissolution of zeolite components with alkali treatment brought about significant changes in the morphology of zeolites as well as their crystalline phases. Fig. 3 shows SEM photos of the alkali-treated natural zeolites. The NZ(0) zeolite did not have large pores. On the other hand, a small number of large holes appeared on the BNZ(4.0) zeolite due to the dissolution of zeolite components. Alkali treatment with more concentrated NaOH solutions caused a considerable change in pore structure, producing a sponge-like material connected with large hole population. As alkaline solution dissolves silica and alumina simultaneously, the alkali treatment of natural zeolites at a proper concentration is helpful in forming large pores suitable for the diffusion of large molecules.

Natural zeolites usually contain several contaminants, other than the zeolite components. The change in chemical composition with alkali treatment gives some information about the removal of the contaminants and the dissolution of the zeolite components. As listed in Table 1, the chemical composition of the BNZ(1.0) zeolite was quite different from that of the NZ(0) zeolite. The alumina content was not considerably changed with an alkali treatment of 1.0 N NaOH solution, but the silica content was significantly increased. More significant changes were observed in the contents of alkaline and alkaline metal oxides; most of them were removed by alkali treatment. This means that an alkali treatment with 1.0 N NaOH solution is sufficient to remove the contaminants, because most of the contaminants are carbonates and chlorides of alkaline and alkaline earth metals. By contrast, alkali treatments with strong NaOH solutions, above 4.0 N, brought about massive silica dissolution. The removal of alumina and other components was relatively small compared with silica, so the Si/Al molar ratios of the alkali-treated natural zeolites declined to 3.0 in the BNZ(8.0) zeolite. Since the Si/Al molar ratio of the typical mordenite is 5, the low Si/Al molar ratio indicates a strong loss of mordenite when treated with concentrated NaOH solutions. Removal of impurities, as well as zeolite components, by alkali treatment, therefore considerably lowers the recovery percentage after treatment with a concentrated alkaline solution.

The pore structures of the alkali-treated natural zeolites also vary greatly according to the concentration of the alkaline solution. Alkali treatment using a dilute solution may remove only the contaminants, resulting in a considerable opening of zeolite pores. On the other

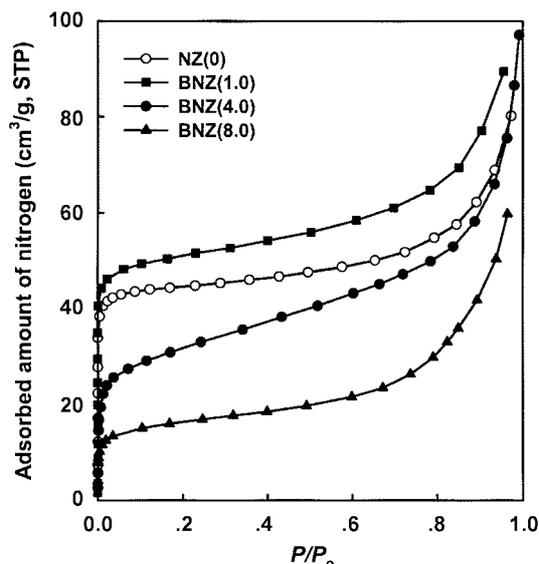


Fig. 4. Nitrogen adsorption isotherms of alkali-treated natural zeolites.

hand, alkali treatment with a concentrated solution dissolves zeolite skeletons, exhibiting a significant loss of zeolite pores. Fig. 4 shows the nitrogen adsorption isotherms of the alkali-treated natural zeolites. The amount of nitrogen adsorbed on the BNZ(1.0) zeolite was larger than that of the NZ(0) zeolite, indicating an increase in zeolite pores. By contrast, a further increase in the concentration of NaOH solution brought about considerable decreases in the amount of nitrogen adsorbed, illustrating a dissolution of the zeolite components. Since the gradual increase in the slope of nitrogen adsorption isotherms at 0.2-0.8 of P/P_0 is related to the presence of mesopores, it is clear that most of the zeolite pores are dissolved on the BNZ(4.0) and BNZ(8.0) zeolites. Overall, alkali treatment with a 1.0 N NaOH solution is effective in removing contaminants, resulting in an increase of zeolite pores.

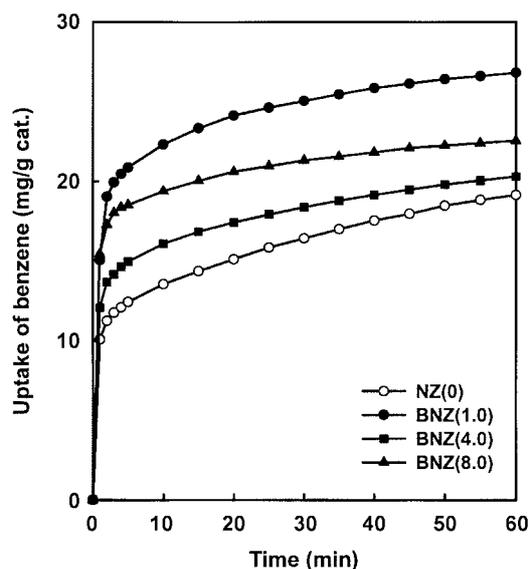


Fig. 5. Uptake curves of benzene on alkali-treated natural zeolites.

Although the dissolution of zeolite components by alkali treatments causes a loss of micropores, the formation of mesopores and macropores induces an increase in both adsorption rate and adsorbed amount of large molecules. As shown in Fig. 5, the uptake amount of benzene on the BNZ(1.0) zeolite increased considerably compared to that on the NZ(0) zeolite. Furthermore, rapid approaches to adsorption equilibrium of benzene on the BNZ(4.0) and BNZ(8.0) zeolites indicated a considerable increase in the adsorption rate of benzene. Such a rapid increase is responsible for the formations of mesopores and macropores during alkali treatment. The uptake amount of benzene on the alkali-treated natural zeolites, however, was not proportional to the concentration of NaOH solution, because mesopores and macropores were randomly formed. Nevertheless, alkali treatment was found to be effective in enlarging the pores of the natural zeolites, suitable for easy access of large molecules, even though enlargement is caused by the dissolution of the zeolite components.

Alkali treatment of the natural zeolites with a dilute solution was helpful in enhancing its adsorption capacity, but the number of acid sites measured by ammonia adsorption decreases gradually with the increase in the concentration of the used NaOH solution. As shown in Fig. 6, TPD profiles of ammonia showed a gradual decrease of the amount of ammonia adsorbed by alkali treatment. The *l*- and *h*-peaks, conventionally attributed to weak and strong acid sites, respectively, were simultaneously decreased with alkali treatment. Since most acid sites are distributed on the surface of the zeolite pores, dissolution of the zeolite components by alkali treatment results a gradual decrease in the amount of acid sites.

2. Catalytic Activity of Alkali-treated Natural Zeolites

Thermal degradation at 410 °C without any catalysts yielded only a gas production of 3%, with a negligible formation of liquid products. However, the alkali-treated natural zeolite, the BNZ(4.0) zeolite, showed high degradation activity (Fig. 7). Although the zeolite components, as well as the impurities, were partially dissolved by the alkaline solutions, enhancement in catalytic activity was obvi-

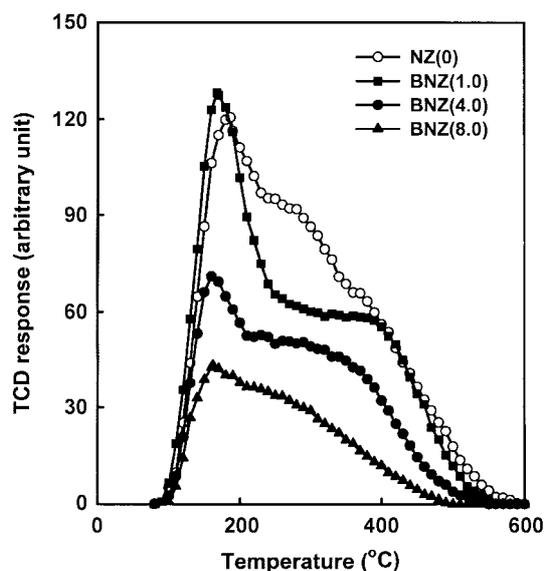


Fig. 6. TPD profiles of ammonia from alkali-treated natural zeolites.

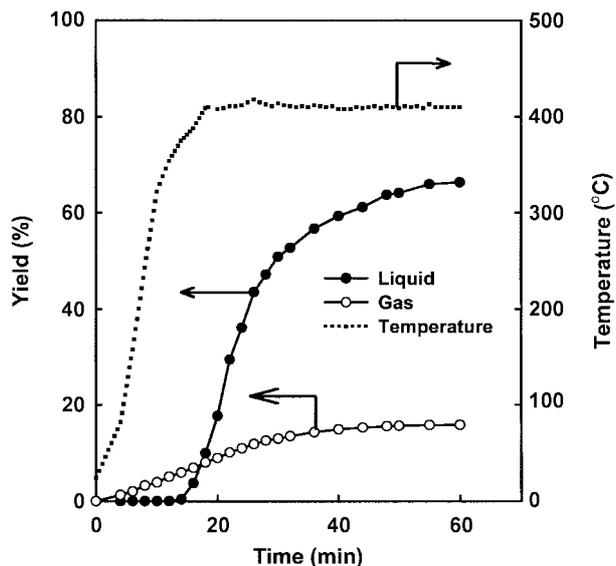


Fig. 7. Catalytic degradation of HDPE over the BNZ(4.0) catalyst at 410 °C.

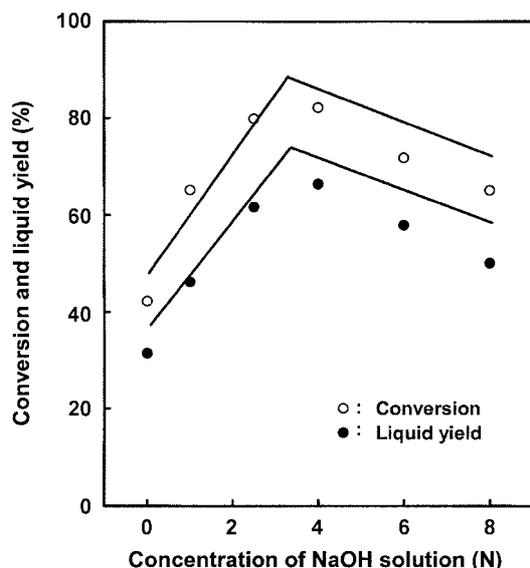


Fig. 8. Variations of the conversion and liquid product yield over alkali-treated natural zeolite catalysts with the concentration of treating NaOH solution. Catalytic activity was determined in the liquid-phase degradation of HDPE at 410 °C.

ous. The variation of catalytic activities after alkali treatment with the concentration of NaOH solution is shown in Fig. 8. Both the conversion and liquid-product yield showed maxima when the concentration of NaOH solution was 4.0 N. On the contrary, the conversions on the NZ(0) and BNZ(8.0) zeolites were relatively low. Since the acid sites of the natural zeolites decrease with an increase in the concentration of NaOH solution, this trend indicates that the number of acid sites is not the only determining factor for catalytic activities.

The adsorbed amounts of benzene and nitrogen on the BNZ(1.0) catalyst were the largest among the alkali-treated natural zeolites, but the highest conversion was obtained on the BNZ(4.0) catalyst.

This means that the density of the acid sites is also important to catalytic activity. A high concentration of acid sites causes rapid deactivation due to rapid carbon deposition. The oligomerization of reactive species is suppressed on the surface of the catalysts with a moderate concentration of acid sites, resulting in a long catalyst life and a high conversion rate. The mordenite catalysts with both the highest and lowest acid site densities showed lower conversions than the mordenite catalyst with a moderate acid site density in liquid-phase degradation of PE wax [You et al., 1999]. The amount of acid sites must therefore be important for catalytic activity in acid-catalyzed degradation reactions, but its density is also important for the catalyst life, especially on catalytic reactions with rapid carbon deposition.

Although HDPE conversions on the alkali-treated natural zeolites varied largely with the concentration of NaOH solutions, the difference in the chemical compositions of gas and liquid products was very small, regardless of the extent of the alkali treatment. The major component of the gas products was C₄ hydrocarbons for all the natural zeolite catalysts tested. The chemical composition of liquid products was also similar, as shown in Fig. 9. The disappearance in higher hydrocarbons, above C₁₄, on the BNZ(1.0) catalyst, might be due to the higher involvement of the zeolite components. The relatively high content of zeolite components reduces the catalytic degradation of HDPE on the external surface, increasing the yield of shorter hydrocarbons.

Alkali treatment has not yet been considered as an efficient method for improving zeolite catalytic activities, because alkali dissolves the zeolite skeleton itself. Natural zeolite treated with concentrated NaOH solutions completely lost its catalytic activity, as well as its zeolite structure. Alkali treatment of natural zeolite with a moderate concentration, however, significantly improved its catalytic activity. A partial dissolution of the zeolite components by alkaline solutions, along with a removal of contaminants, brings about the formation of mesopores, causing a rapid diffusion of large polymeric

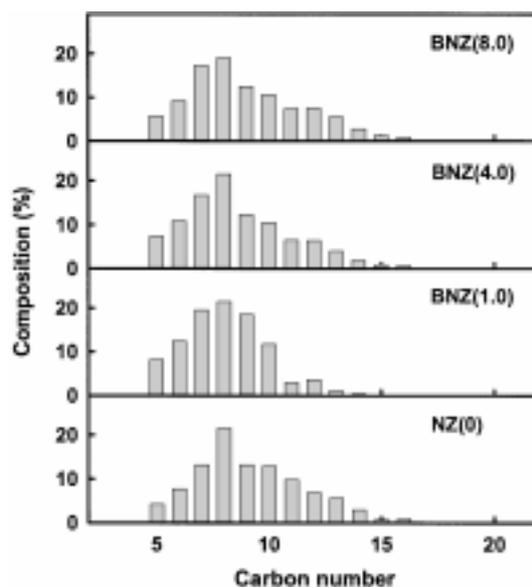


Fig. 9. Compositions of liquid products obtained from the liquid-phase degradation of HDPE over alkali-treated natural zeolite catalysts at 410 °C.

materials. The reduction of acid sites also suppresses the carbon deposition, resulting in longer catalyst lives and higher conversion rates.

CONCLUSIONS

Although natural zeolite itself is not active as a catalyst for the liquid-phase degradation of HDPE, alkali treatment with NaOH solution of moderate concentrations significantly improved its catalytic activity. A partial dissolution of zeolite components produced mesopores, thereby enhancing the diffusion of polymeric materials. The suppression of rapid carbon deposits on the natural zeolite by lowering the acid site densities, also caused longer catalyst lives and higher conversion rates. Alkali treatment with concentrated alkaline solutions, however, brought about severe dissolution of zeolite components, resulting in lower activity.

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