

## Skeletal isomerization of *n*-butenes to isobutene over acid-treated natural clinoptilolite zeolites

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### Abstract

The proton form of the natural clinoptilolite zeolite (HNZ) was modified by treatment with various acids. Effects of modification on catalytic performance were investigated for the skeletal isomerization of *n*-butenes to isobutene. Among HNZs treated with various acids, only those modified with boric acid (B-HNZ) showed an improved catalytic performance of skeletal isomerization in terms of activity and stability. Furthermore, B-HNZ exhibited higher isobutene selectivity compared to unmodified HNZ at the same conversion of *n*-butenes. The performance was comparable to that of a widely known ferrierite catalyst at the same reaction conditions. The main effect of boric acid treatment on HNZ was the selective increase in the number of acid sites of moderate strength required for efficient catalysts in skeletal isomerization without collapse of its framework. These acid sites of moderate strength were considered to be selective and stable reaction sites for skeletal isomerization of *n*-butenes. Coke deposition poisoned non-selective strong acid sites and imposed a spatial restriction on zeolite channels, leading to suppression of undesired dimerization reactions. Factors affecting selectivity to isobutene are discussed. ©2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Clinoptilolite; Skeletal isomerization; Acidity; Selectivity; Coke deposition

### 1. Introduction

Isobutene is a main raw material for the manufacture of the methyl-tertiary-butyl ether (MTBE), widely used as an octane booster for reformulated gasoline [1]. There also are various applications of isobutene as a chemical intermediate for industrial products. The current primary source of isobutene is C<sub>4</sub> raffinate of catalytic cracking fractions. Since the demand for

MTBE has continuously increased, considerable interest has been devoted to finding a new, independent source of isobutene. The catalytic skeletal isomerization of *n*-butenes to isobutene is the most promising way for the production of isobutene that could satisfy the increased demand for isobutene [2].

Recently, various zeolite and molecular sieve catalysts have been applied to skeletal isomerization of *n*-butenes as efficient catalysts, and studied extensively [3–8]. The common features shared by these efficient zeolite catalysts are proper acid strength, pore size and unique pore structure with a 10-membered ring [9,10]. Clinoptilolite, employed as a catalyst in this

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study, has a pore structure of a monoclinic framework consisting of a 10-membered ring ( $7.6 \times 3.0 \text{ \AA}$ ) and an 8-membered ring ( $3.3 \times 4.6 \text{ \AA}$ ), and is a silica-rich member of the heulandite family [11].

In our previous study [12], we reported that natural clinoptilolite zeolite produced in the Youngil area of South Korea was an effective catalyst for skeletal isomerization.

In the present study, we modified the natural clinoptilolite zeolite by reflux and impregnation with various acids, such as boric acid, phosphoric acid and nitric acid, in order to identify the role of the acidity in skeletal isomerization of *n*-butenes to isobutene. We also compared modified natural clinoptilolite zeolites with ferrierite, known as the most efficient catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

A natural zeolite (NZ) occurring in the Youngil area of South Korea was employed to obtain the proton-form natural zeolite catalyst (HNZ) by an ion-exchange method. Thus the natural zeolite was ion-exchanged four times with 1 M aqueous solution of  $\text{NH}_4\text{Cl}$  (25 ml solution per gram of NZ) at  $80^\circ\text{C}$  for 24 h, and the resulting catalyst, the ammonium form ( $\text{NH}_4^+$ ) of the natural zeolite, was filtered, washed several times with clean distilled water, dried at  $110^\circ\text{C}$  for 20 h, and then calcined at  $500^\circ\text{C}$  for 4 h in air. By this procedure, the proton form natural zeolite, HNZ, was prepared.

In order to modify the acidity, HNZ was refluxed with various concentrations of acidic solutions, such as  $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HNO}_3$ , at  $95^\circ\text{C}$  for 0.5–5 h. HNZ was also impregnated with various amounts of boric acid or phosphoric acid by an incipient wetness method. The acid-treated catalysts were dried at  $110^\circ\text{C}$  and calcined at  $500^\circ\text{C}$  for 4 h in air before catalytic reactions. The modified natural clinoptilolite zeolites were denoted as B-HNZ, P-HNZ and N-HNZ for HNZ treated with  $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HNO}_3$ , respectively. We also tested ferrierite ( $\text{Si}/\text{Al} = 16.9$ , surface area =  $214.1 \text{ m}^2/\text{g}$ ) which was synthesized according to the procedure described in the literature [13] in order to compare it with acid-treated HNZ.

### 2.2. Catalyst characterization

The bulk structure of HNZ and modified HNZs was confirmed by XRD (MAC Science Co, M18XHF) analysis with  $\text{Cu K}\alpha$  radiation. The  $\text{Si}/\text{Al}$  ratio was determined by atomic absorption spectroscopy (Perkin–Elmer AAS 5100 PC). The surface area of the catalysts was measured by a BET surface analyzer (Micrometric Co, Accusorb 2100E).

The amount of coke deposited after reaction was measured on a CHNS analyzer (LECO Co, CHNS-932). Temperature-programmed oxidation (TPO) with 1%  $\text{O}_2$  balanced with helium was also carried out for used catalysts in order to probe the degree of coking. The sample, typically 20 mg, was heated from room temperature (RT) to  $900^\circ\text{C}$  at a temperature ramping rate of  $10^\circ\text{C}/\text{min}$  and the desorbed  $\text{CO}_2$  was monitored by a mass spectrometer (HP5972 MSD).

The acidity of the modified catalysts was determined by temperature-programmed desorption (TPD) of ammonia. The catalysts were treated in He flow of  $44.6 \mu\text{mol}/\text{s}$  at  $500^\circ\text{C}$  for 1 h and then cooled to room temperature.  $\text{NH}_3$  was adsorbed on the catalysts by flowing  $\text{NH}_3$  at  $100^\circ\text{C}$  for 0.5 h and the physisorbed species were removed by purging the sample with He flow for 1 h. The temperature ramping rate was  $10^\circ\text{C}/\text{min}$  from 100 to  $900^\circ\text{C}$  and the desorbed  $\text{NH}_3$  was monitored by a mass spectrometer (HP5972 MSD).

### 2.3. Catalytic reactions

The skeletal isomerization of *n*-butenes to isobutene was carried out in a continuous fixed-bed flow reactor at atmospheric pressure. The catalysts, typically 0.5 g, were heated from RT to  $500^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  in  $\text{H}_2$  flow and then kept at  $500^\circ\text{C}$  for 1 h. After the pre-treatment of the catalysts, the temperature was adjusted to a desired reaction temperature. The stream of *n*-butenes (Matheson) was fed to the reactor at a rate of  $3.7 \mu\text{mol}/\text{s}$ . The total flow rate including diluent gas was maintained at  $18.6 \mu\text{mol}/\text{s}$ . The reactant flow rate was expressed by WHSV [ $\text{h}^{-1}$ ] defined as  $\text{g}_{\text{C}_4 \text{ feed}}/\text{g}_{\text{cat}}/\text{h}$ . The reaction products were analyzed by an on-line gas chromatograph (Hewlett Packard 5890 series II) equipped with a flame ionization detec-

tor and a column of 20% BMEA (24 ft long, supplier: Craw).

The conversion was calculated from the consumed *n*-butenes and the selectivity to isobutene was obtained by dividing moles of effluent isobutene by those of consumed *n*-butenes. In the present study, 2-butenes were considered as reactants, since rapid double-bond isomerization between 1-butene and 2-butenes was established at reaction temperatures covered in the present work and 2-butenes could also be isomerized to isobutene.

### 3. Results

#### 3.1. Characterization of acid-treated HNZ

The proton form of the natural clinoptilolite zeolite (HNZ) was modified by various acid treatments in order to investigate the effect of acidic properties on skeletal isomerization of *n*-butenes into isobutene. Modified HNZ catalysts were prepared in two ways: impregnation and reflux methods. In those methods, only samples prepared by reflux showed good activity for skeletal isomerization.

The physicochemical properties of fresh HNZ and modified catalysts by reflux are shown in Table 1. As the strength of employed acid became greater, the Si/Al ratio increased and at the same time the surface area decreased to a greater extent. Among acid-treated HNZs, only HNZ modified with boric acid (B-HNZ) showed an improved yield of isobutene, compared to

Table 1  
Physicochemical properties HNZ and acid-treated HNZs and the yield of isobutene

Catalyst	Si/Al ratio	BET surface area (m <sup>2</sup> /g)	Yield <sup>a</sup>
HNZ	4.62	221.3	30.44
B-HNZ <sup>b</sup>	4.64	194.1	35.15
P-HNZ <sup>c</sup>	12.38	183.5	14.85
N-HNZ <sup>d</sup>	15.08	162	–

<sup>a</sup> Yield of isobutene after 5 h of the reaction at 450°C (WHSV = 1.5 h<sup>-1</sup>, H<sub>2</sub>/C<sub>4</sub> = 4).

<sup>b</sup> Boric acid-treated HNZ (2 M aqueous solution of H<sub>3</sub>BO<sub>3</sub> at 95°C for 5 h), 0.07 wt% B.

<sup>c</sup> Phosphoric acid-treated HNZ (1 M aqueous solution of H<sub>3</sub>PO<sub>4</sub> at 95°C for 0.5 h).

<sup>d</sup> Nitric acid-treated HNZ (1 M aqueous solution of HNO<sub>3</sub> at 95°C for 5 h).

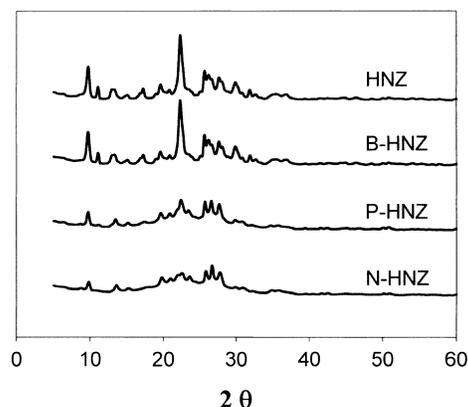


Fig. 1. X-ray diffraction patterns of various acid treated HNZs: boric (B), phosphoric (P) and nitric (N) acid treatments.

untreated HNZ. On the contrary, P-HNZ exhibited poor activity and N-HNZ was totally inactive for skeletal isomerization. For the case of impregnation, it was observed that the surface area was reduced greatly. When HNZ was impregnated with boric or phosphoric acid in the amount of 1 wt%, the measured surface areas were 15.5 and 43.3 m<sup>2</sup>/g, respectively.

In order to examine the change in the pore structure due to de-alumination in acid-treated HNZs, the XRD patterns of samples are shown in Fig. 1. The HNZ was identified to be clinoptilolite [11]. There seems to be little change in the structure of the clinoptilolite when treated with boric acid. The intensity of the main peak of B-HNZ was increased slightly. On the other hand, P-HNZ and N-HNZ showed severely reduced peak intensities. Thus, as the extent of de-alumination of the framework was excessive, the structure of HNZ was liable to be destroyed.

Fig. 2 shows NH<sub>3</sub>-TPD profiles of acid-treated HNZs, unmodified HNZ, and FER. The temperature of the peak maximum reflects the acid strength, although the re-adsorption of desorbed ammonia may shift the temperature to a higher temperature [14,15]. Fig. 2A represents NH<sub>3</sub>-TPD profiles of fresh HNZ and catalysts modified by phosphoric or nitric acids. The absolute number of both weak and strong acid sites is reduced by the treatments; this effect was more severe for nitric acid treatment. There was little change in acid strength by these treatments, as indicated by no change in peak temperatures. Together with data listed in Table 1, we concluded that acid treatments by H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub> cause de-alumination

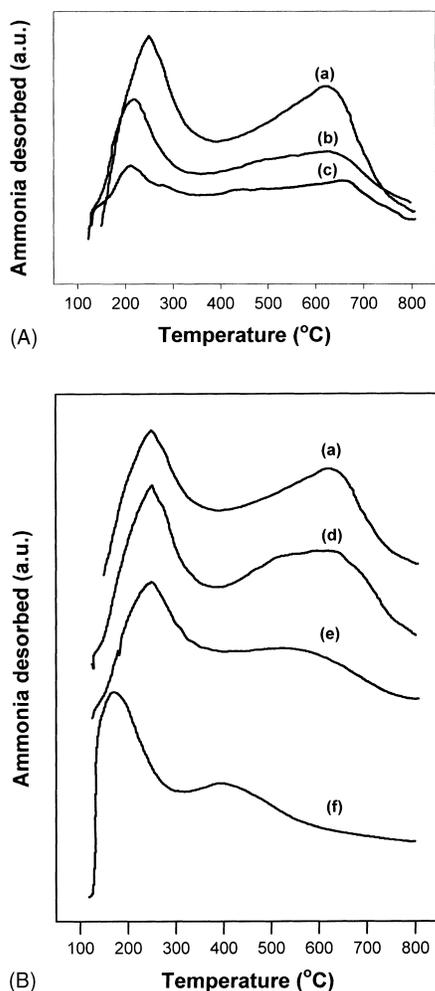


Fig. 2. (A) TPD of ammonia for various acid-treated HNZs: (a) HNZ, (b) P-HNZ, (c) N-HNZ, (B) TPD of ammonia: (a) HNZ, (d) B-HNZ before the reaction, (e) B-HNZ after the reaction, (f) ferrierite.

and reduction in the number of acid sites without change in their nature.

$\text{NH}_3$ -TPD profiles of HNZ, B-HNZ and ferrierite are compared in Fig. 2B. For the case of B-HNZ, the total number of acid sites was increased (Fig. 2d). Particularly, the increase in the number of acid sites with moderate acid strength, represented by  $\text{NH}_3$  desorption at temperatures of 400–550°C, was much greater than that of other acid sites. Most of these moderate acid sites still remained after the reaction, while stronger acid sites mostly disappeared (Fig. 2e). It is

interesting to note that ferrierite, an excellent catalyst for skeletal isomerization of *n*-butenes, also possessed acid sites of a moderate strength (Fig. 2f).

### 3.2. Catalytic performance of acid-treated HNZ

B-HNZ catalyst prepared from natural clinoptilolite zeolite has shown excellent activity and stability in the skeletal isomerization of *n*-butenes to isobutene. Fig. 3 shows skeletal isomerization of *n*-butenes over B-HNZ at various reaction temperatures with  $\text{H}_2$  as a diluent gas. Conversion of 1-butene was high and stable at 450°C, while it decreased rapidly at higher temperatures. Selectivity to isobutene increased as the reaction temperature and also time-on-stream were raised. At 450°C, the best yield of ca. 36% was obtained and good stability was maintained with time-on-stream. At higher temperatures, however, the catalyst showed de-activation but higher selectivities.

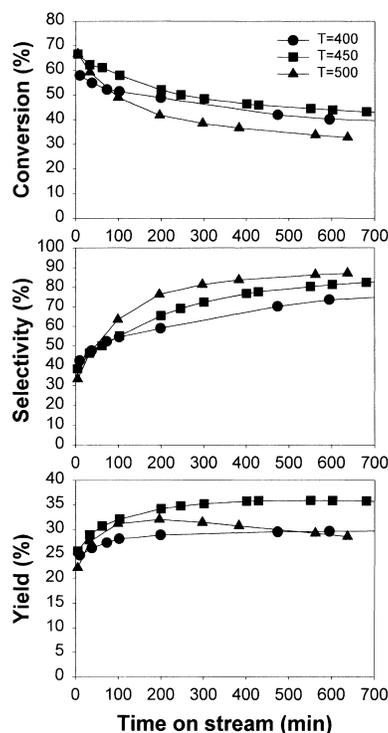


Fig. 3. Influence of the reaction temperature upon 1-butene conversion, selectivity to isobutene and yield of isobutene over B-HNZ as a function of time-on-stream. Reaction conditions: atmospheric pressure,  $\text{WHSV} = 1.5 \text{ h}^{-1}$ ,  $\text{H}_2/\text{C}_4 = 4$ .

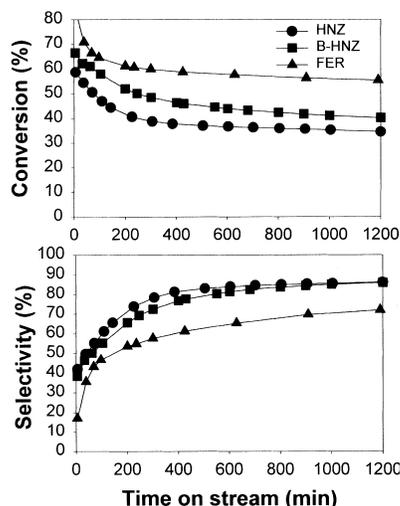


Fig. 4. Comparison of the catalytic activity over HNZ, B-HNZ and ferrierite as a function of time on stream. Reaction conditions:  $T=450^{\circ}\text{C}$ , atmospheric pressure,  $\text{WHSV} = 1.5\text{ h}^{-1}$ ,  $\text{H}_2/\text{C}_4 = 4$ .

However, the de-activation was less severe than HNZ. The de-activation of the catalyst has been known to be due to coke formation. It is also agreed that coke deposited on the catalyst exerts a positive effect of improved selectivity [16]. Coke deposition will give rise to more spatial restriction to zeolite channels and suppression of the dimerization reaction, the main competitive side reaction, that produces  $\text{C}_3$  (propenes) and  $\text{C}_5$  (pentenes) products by subsequent cracking.

B-HNZ was compared with HNZ and ferrierite under the same reaction conditions of  $450^{\circ}\text{C}$ ,  $\text{WHSV} = 1.5\text{ h}^{-1}$  and  $\text{H}_2/\text{C}_4 = 4$ . As revealed in Fig. 4, B-HNZ shows better activity than HNZ. Selectivity was somewhat lower. However, when compared at the same conversion of  $n$ -butenes, B-HNZ exhibited higher selectivity than that of HNZ. At this temperature, both HNZ and B-HNZ showed good stability with time-on-stream. Ferrierite showed good activity and stability with time-on-stream, although selectivity was lower than that of HNZ or B-HNZ. Consequently, ferrierite showed the highest yields of ca. 40%, mainly due to high conversions.

Fig. 5 shows catalytic yields over B-HNZ and HNZ at different temperatures under otherwise the same conditions after 10 h reaction and compares them with theoretical yields calculated from thermodynamic equilibrium [17]. B-HNZ showed higher yields by ca. 20% compared with HNZ and these yields

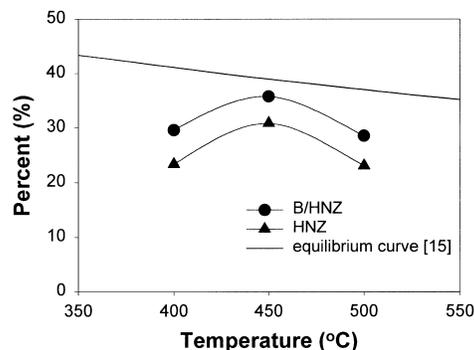


Fig. 5. The temperature dependence of the yield of isobutene over HNZ and B-HNZ after 10 h reaction. Reaction conditions: atmospheric pressure,  $\text{WHSV} = 1.5\text{ h}^{-1}$ ,  $\text{H}_2/\text{C}_4 = 4$ .

for isobutene were not far from the thermodynamic equilibrium.

Product distributions of the skeletal isomerization of  $n$ -butenes at the time-on-stream of 5 h over HNZ, B-HNZ, P-HNZ and ferrierite are shown in Table 2. The low selectivity of ferrierite was attributed mainly to the formation of  $\text{C}_3$  and  $\text{C}_5$  by-products. In the case of P-HNZ, conversion was much lower and selectivity was also slightly lower compared with HNZ. Rapid de-activation of the catalyst was also observed. Both HNZ and B-HNZ showed higher selectivities than ferrierite without loss of stability.

Table 2

Product distribution of skeletal isomerization of  $n$ -butenes to isobutene at time on stream 5 h over HNZ, B-HNZ, P-HNZ and ferrierite<sup>a</sup>

Catalysts→products↓	HNZ	B-HNZ	P-HNZ	ferrierite
$\text{C}_1$	0.45	0.72	0.11	0.48
$\text{C}_2$	0.83	1.61	0.22	1.80
$\text{C}_3$	3.36	5.18	1.83	10.85
Isobutane	0.59	1.18	0.32	2.81
$n$ -butane	0.86	1.69	0.56	2.61
I-butene	10.95	8.98	18.66	6.17
Iso-butene	30.39	35.08	14.82	34.26
<i>Trans</i> -2-butene	28.52	24.15	34.62	18.98
<i>Cis</i> -2-butene	21.64	18.27	26.96	14.62
Heavier ( $\text{C}_{5+}$ )	2.42	3.15	1.89	5.59
<i>Trans/Cis</i>	1.32	1.32	1.28	1.30
Conversion (%)	38.78	48.51	19.59	59.96
Selectivity (%)	78.51	72.46	75.77	57.59
Yield (%)	30.44	35.15	14.85	34.31

<sup>a</sup> Reaction conditions:  $T=450^{\circ}\text{C}$ .  $\text{WHSV} = 1.5\text{ h}$ ,  $\text{H}_2/\text{C}_4 = 4$ , atmospheric pressure.

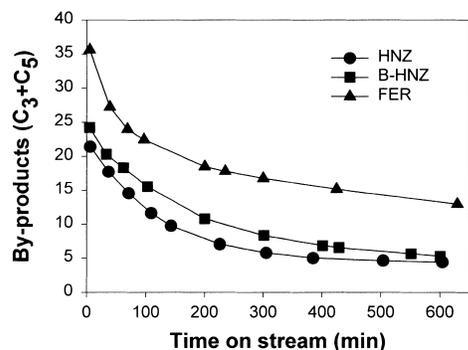


Fig. 6. Comparison of the by-products ( $C_3 + C_5$ ) produced over HNZ, B-HNZ and ferrierite at a constant flow rate ( $WHSV = 1.5 h^{-1}$ ) as a function of time on stream. Reaction conditions:  $T = 450^\circ C$ , atmospheric pressure,  $H_2/C_4 = 4$ .

Fig. 6 shows comparison of the by-products ( $C_3 + C_5$ ) over HNZ, B-HNZ, and ferrierite at constant flow rate ( $WHSV = 1.5 h^{-1}$ ) as a function of time-on-stream. It can be confirmed that ferrierite generates the largest amount of by-products. Thus, dimerization and cracking is competitive to skeletal isomerization of *n*-butenes for ferrierite. By-products for B-HNZ decreased gradually to the same level of HNZ at the time on stream of 10 h.

In order to investigate the effects of carbonaceous deposition on improved selectivity into isobutene, TPO of used catalysts was carried out. Fig. 7 represents TPO profiles of HNZ and B-HNZ after reaction of 10 h. The amount of desorbed  $CO_2$  from B-HNZ was similar to that of HNZ. In Fig. 8, the amount of coke deposited on the catalysts after reaction is compared with selectivity to isobutene. The correla-

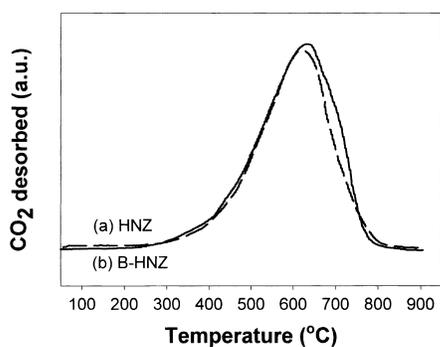


Fig. 7. TPO profiles of HNZ and B-HNZ after 10 h of the reaction: (a) HNZ, (b) B-HNZ.

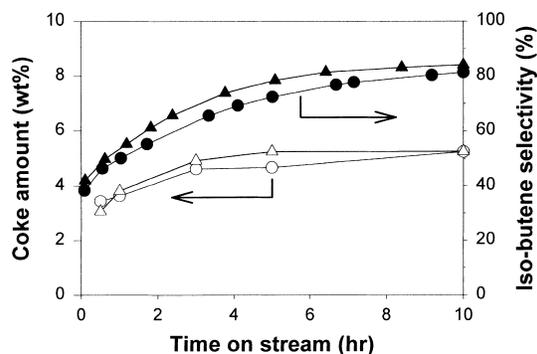


Fig. 8. The amount of coke deposition and selectivity to isobutene for HNZ and B-HNZ as a function of time on stream: (●) B-HNZ, (▲) HNZ. Reaction conditions: atmospheric pressure,  $T = 450^\circ C$ ,  $WHSV = 1.5 h^{-1}$ ,  $H_2/C_4 = 4$ .

tion between the two properties is good. Both HNZ and B-HNZ showed increases in selectivity as coking proceeded.

#### 4. Discussion

In the present study, we have modified the proton form of the natural clinoptilolite zeolite (HNZ) by acid treatment and investigated its effects on catalytic properties for skeletal isomerization of *n*-butenes to isobutene. Among acid-treated HNZ, only B-HNZ showed improved activity and stability. Its performance was comparable to ferrierite, known as one of the best catalysts.

In general, it has been known that unique pore structure, proper acidity, and acid site distribution are essential for the selective skeletal isomerization of *n*-butenes. Recently, Houžvička et al. [9] investigated shape selectivity in the skeletal isomerization of *n*-butenes to isobutene over several microporous materials to elucidate the most appropriate pore structure. The authors reported that 10-membered ring (10MR) zeolites had the most suitable pore structure with the pore diameter of 4.0–5.5 Å. For 8-membered ring (8MR) zeolites, diffusion of isobutene is sluggish due to small pore size and carbonaceous deposition occurs very quickly on their external surface. 12-membered ring zeolites are not able to suppress the formation of carbonaceous deposits effectively.

Indeed, effects of pore structure on the skeletal isomerization of *n*-butenes are significant.

Among the 10-membered ring zeolite catalysts, ferrierite-containing 10-membered rings ( $4.2 \times 5.4 \text{ \AA}$ ) intersected by 8-membered rings ( $3.5 \times 4.8 \text{ \AA}$ ) have exhibited the best activity and stability reported to date [18]. Although the reason for the best catalytic performance of ferrierite in skeletal isomerization of *n*-butenes is not clearly understood, it may be attributed to more a favorable diffusion of butenes [10].

Our catalyst, natural clinoptilolite, also has pore channels of 10MR and 8MR. We have already demonstrated that HNZ is an efficient catalyst for the skeletal isomerization of *n*-butenes to isobutene [12]. In the present study, natural clinoptilolite modified by boric acid treatment exhibits improved activity and yield of isobutene, giving the best yield of ca. 36%. HNZ and B-HNZ are compared to ferrierite at the same reaction conditions as shown in Fig. 4. Although ferrierite exhibited better activity, selectivity for isobutene was much less than that of B-HNZ for the whole time-on-stream. B-HNZ also showed excellent stability as a function of time-on-stream. The low selectivity of ferrierite was due to the formation of by-products, as shown in Table 2. The major by-products were C<sub>3</sub> (propenes) and C<sub>5</sub> (pentenes), which were formed from dimerization of *n*-butenes followed by cracking. As can be seen in Fig. 6, the amount of by-products over ferrierite is much larger than that over B-HNZ.

In a recent study, Seo et al. [19] used a synthetic clinoptilolite zeolite as a catalyst in the skeletal isomerization of 1-butene. The authors have shown that adsorption of 1-butene molecules on clinoptilolite zeolite is more restricted to very specific sites than on ferrierite from the simulated distribution of adsorbed 1-butene molecules. They also calculated potential energy profiles for a 1-butene molecule and showed a high potential barrier of the 1-butene molecule in the 10-membered ring channels of clinoptilolite zeolite. The higher selectivity of clinoptilolite zeolite resulted from a more severe spatial constraint of its pores.

Therefore, differences in selectivity between clinoptilolite and ferrierite appear to be due to the relative pore size and shape. That is, relatively narrower 10-membered ring channels of clinoptilolite and wider 10-membered pore channels of ferrierite affect diffusion characteristics of *n*-butenes into the respective pores. It is likely that ferrierite has a higher proba-

bility of having two *n*-butene molecules next to each other in the zeolite pores to affect dimerization, while the probability for clinoptilolite zeolites is less. For the case of B-HNZ, the steric constraint of the clinoptilolite structure should be effective in addition to the effect that the acid treatment might have.

For the method of acid treatment, impregnation with the acid to incipient wetness was not effective in the modification of HNZ. It caused drastic reduction in surface area. Thus, the reflux method should be the choice of acid treatment to obtain a catalyst active for the skeletal isomerization of *n*-butenes.

Our results indicate that the main effect of acid treatment of HNZ is an effective modification of its acid characteristics, especially by boric acid treatment. The boric acid treatment not only maintains the pore structure of the clinoptilolite zeolite, but also increases the number of moderate acid sites selectively. These conclusions are supported by the XRD pattern (Fig. 1) and the NH<sub>3</sub>-TPD profile (Fig. 2B) of B-HNZ. B-HNZ improves the performance of skeletal isomerization of *n*-butenes in terms of activity and stability. Furthermore, selective increase of moderate acid sites in B-HNZ leads to a slightly higher selectivity than that of HNZ when compared at the same conversion of *n*-butenes. Therefore, these moderate acid sites are considered to be selective reaction sites for the skeletal isomerization of *n*-butenes to isobutene. Indeed, it has been suggested that moderate Brønsted acid sites are the active sites for skeletal isomerization of *n*-butenes, while strong acid sites induce by-products via dimerization followed by cracking [20].

As shown in Table 2, the reduced number of acid sites accompanied by severe de-alumination for P-HNZ leads to a marked decrease in activity but to a relatively higher selectivity. Dimerization-cracking reactions are suppressed by the decrease in acid sites. It can be supposed that lower density of acid sites is responsible for the suppression of dimerization requiring two adjacent *n*-butene molecules. Thus, selectivity is affected by the number of neighboring acid sites which would contribute to the dimerization reaction, leading to by-products.

No activity was observed for N-HNZ. The severe de-alumination also affected crystallinity as well as acidity. The loss of activity could be attributed to the collapse of the zeolite structure, resulting in the loss of most of the acid sites, as indicated in Figs. 1 and 2A.

Coke deposition induces improvement of selectivity to isobutene and the effect is accelerated as temperature increases. Although coke formation causes the de-activation of the catalysts, the positive effect on selectivity is confirmed by similar patterns of selectivity and coking against the time-on-stream, as shown in Fig. 8. Therefore, it can be said that coke deposited on the catalyst poisons strong acid sites which are considered to be non-selective reaction sites. It also imposes a spatial restriction on zeolite channels, leading to suppression of undesired dimerization followed by cracking to C<sub>3</sub> and C<sub>5</sub>.

To summarize the above considerations, it can be concluded that the first factor in determining catalytic performance for skeletal isomerization of *n*-butenes to isobutene is the unique pore structure, especially having 10-membered ring channels that lead to shape selectivity. In addition, another important factor which affects activity and selectivity for zeolites with the similar pore structure is their acid characteristics. Selective increase in the population of moderate acid sites and selective poisoning of strong acid sites that are responsible for the side reaction like dimerization-cracking, are essential for selective skeletal isomerization of *n*-butenes. The treatment of HNZ by boric acid has achieved this goal. Furthermore, acid site distribution suppressing the bimolecular reaction and allowing effective steric constraints is also a crucial factor to improve selectivity to isobutene, as inferred from the higher selectivity of clinoptilolite relative to ferrierite.

## 5. Conclusions

Among various acid treatments of natural clinoptilolite, only boric acid treatment by the reflux method shows improved performance of skeletal isomerization of *n*-butenes to isobutene. The boric acid-treated natural zeolite shows higher selectivity to isobutene, as compared to the untreated zeolite at the same conversion of *n*-butenes. The performance was comparable to ferrierite at the same reaction conditions. Though ferrierite exhibits good activity, selectivity to isobutene is much lower than that of modified natural zeolite. The main effect of boric acid treatment is the selective increase in the number of moderate acid sites without collapse of its framework. These moderate acid sites

are considered to be selective reaction sites for skeletal isomerization of *n*-butenes. The role of coke deposition is to poison strong acid sites which are regarded as non-selective sites, as well as to impose a spatial restriction on zeolite channels, leading to suppression of undesired dimerization.

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