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Selective production of isobutylene from acetone over alkali metal ion-exchanged BEA zeolites

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ABSTRACT

Selective production of isobutylene from acetone was examined over BEA zeolites. Isobutylene production from acetone proceeds over solid-acid catalysts via a series of consecutive reactions, which include propylene and ethylene formation by cracking and coke formation. Because the isobutylene is an intermediate chemical in this process, low diffusion resistance of the isobutylene within the pore of the catalyst is needed to prevent its further conversion. To achieve this goal, we selected a BEA-type zeolite with 12-membered rings and a 3-dimensional pore structure. To obtain high yields of isobutylene, it is also important to inhibit undesired reactions of isobutylene and other intermediates that produce aromatics and coke. In this study, the acidity of the BEA zeolites was controlled using an ion-exchange method with alkali metals. The order of catalytic activity of the ion-exchanged BEA zeolites is as follows: H-BEA, Na-BEA, K-BEA, Rb-BEA, Cs-BEA, and is the same as the order of acidity of the zeolites. Though H-BEA zeolite showed a high acetone conversion at an initial reaction time, the activity of the catalyst drastically decreased due to coke formation. In contrast, the alkali metal ion-exchanged BEA zeolites exhibited high isobutylene selectivity at high acetone conversion conditions. Moreover, the amount of coke deposited on the catalyst decreased as compared to H-BEA zeolite. In K-BEA zeolite, the isobutylene yield reached 55%.

1. Introduction

Zeolites, crystalline aluminosilicate materials, possess strong activity, high surface area, high thermal stability and a high adsorption capacity for hydrocarbons. The sizes of the intracrystalline pores and nanospaces depend on the type of zeolite and are close to the molecular diameters of lighter hydrocarbons. Zeolites thus exhibit a remarkable molecular sieving effect for these hydrocarbons. Hence, they have been widely used as shape-selective catalysts in various types of hydrocarbon processing, e.g., oil refining and olefin synthesis from methanol.

As a feedstock for methyl methacrylate, butyl rubber and ethyl tertiary-butyl ether (ETBE), isobutylene is one of the most important lighter olefins. Recently, due to an increase in demand for isobutylene as well as depletion of energy sources, a new chemical process to produce isobutylene is required. A large amount of acetone is obtained as a by-product in the commercial cumene process. Moreover, acetone is selectively produced from biomass-derived tar (nonedible biomass such as sewage sludge [1] and fermentation residue [2]) using an iron oxide composite catalyst. Accordingly, olefin synthesis from acetone over solid-acid catalysts has been investigated, in which olefins such as ethylene, propylene and isobutylene are produced from decomposition of aldol-condensation products of acetone [3–5]. In these olefin syntheses, selective formation of lighter olefins occurs due to the molecular sieving effect of the zeolite. We have also reported olefins synthesis from acetone over MFI (ZSM-5) zeolite [6]. However, because the pore size of MFI zeolite is relatively small, propylene and ethylene are preferentially produced. Accordingly, zeolites with larger pore sizes than that of MFI zeolite are needed in order to produce isobutylene from acetone.

Because isobutylene is an intermediate chemical in above-mentioned series of reactions, low diffusion resistance of the isobutylene within the pores of the catalyst is required. Compared to MFI-type zeolite, the BEA-type zeolite has large pore size composed of 12-membered rings. Accordingly, we selected BEA-type zeolite as the catalyst, and attempted to develop a new synthesis method for isobutylene from acetone over BEA zeolite. The main objective of this study was selective production of isobutylene from acetone at high yield. The effects of acidity on catalytic

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activity, isobutylene selectivity and coke formation were also investigated.

2. Experimental

Proton-type BEA (H-BEA, Si/Al ratio of 13.5 (HSZ-930NHA) and 250 (HSZ-980HOA), Tosoh Co. Ltd.) and alkali metal ion-exchanged BEA (Na-, K-, Rb- and Cs-BEA, Si/Al ratio of 13.5) zeolites were used as catalysts. Powderly BEA zeolites were treated with ammonium nitrate solutions (0.6 mol/L) to obtain NH_4-BEA zeolite, followed by calcination under an air flow at 773 K, where NH_4-BEA zeolite changed into H-BEA zeolite. The alkali metal ion-exchanged BEA zeolites were obtained using a typical ion exchange method, where 5 g of H-BEA zeolite powder was put in a solution of alkali metal nitrate (0.6 mol/L) with magnetic stirring at 70 °C for 3 h. The ion-exchange treatments were repeated 3 times. After separating the ion-exchanged zeolite from the solution by filtration, it was washed with distilled water, dried at 373 K overnight, and calcined under an air flow at 773 K. The amount of alkali metals loaded on BEA zeolite was analyzed by X-ray fluorescence spectrometer (XRF Supermini, Rigaku Co. Ltd.). The acidity of the ion-exchanged BEA zeolites was measured using the NH_3-TPD method (BELCAT, BEL Japan Co. Ltd.) with 1.0% NH_3 in Ar as a carrier gas, a heating rate of $5\,K\,min^{-1}$ and a temperature range of 373–823 K. The amount of NH_3 molecules desorbed from the acid sites of the zeolite was measured using a Quadrupole mass analyzer (BELMASS, BEL Japan Co. Ltd.) with Ar as the internal standard.

The BEA zeolites described above were pelletized, crushed and sieved to yield samples of ca. 0.3 mm in diameter and then used as catalysts for the synthesis of isobutylene from acetone. The reaction was carried out using a fixed bed-type reactor under a N_2 stream (60 cc/min) at atmospheric pressure and a temperature of 773 K with a W/F (weight ratio of catalyst (g) to acetone feed rate (g/h), h) of 0.5–0.75 kg-cat/(kg-acetone/h). The reaction products were analyzed using online gas chromatography (GC-14A, Shimadzu Corp.) with a Porapak-Q column. The amount of coke deposited on the catalysts after reaction for 6 h was measured by thermogravimetric analysis (TGA-50, Shimadzu Corp.) under an oxygen-nitrogen atmosphere (oxygen: 10%) in the temperature range from 300 to 950 K at a heating rate of $3\,K\,min^{-1}$.

3. Results and discussion

3.1. Olefin synthesis from acetone over BEA zeolites

Fig. 1 shows reaction routes from acetone to olefins over solid-acid catalysts, where isobutylene forms form acetone via a series of reactions. Diacetone alcohol is generated by aldol condensation of two molecules of acetone [7–9], which is an equilibrated reaction. Isobutylene is obtained by decomposition of mesityl oxide produced by dehydration of diacetone alcohol [4,5]. Moreover, isobutylene is also produced by the decomposition of isophorone.

Changes in acetone conversion, product selectivities and olefins composition with time using H-BEA zeolite with different Si/Al ratio (13.5 and 250) at 773 K and a W/F of 0.5 h are shown in Fig. 2. As shown in Fig. 2(a), although the H-BEA with Si/Al ratio of 13.5 exhibited a high acetone conversion in the first 30 min, selectivity was lower for isobutylene than for lighter olefins, such as ethylene and propylene, and aromatics were also produced. Because strong acid sites exist in the H-BEA zeolite, the reactions for producing these lighter olefins and aromatics proceeded readily. In a high silica BEA zeolite shown in Fig. 2(b), although the acetone conversion was low due to low Al content, the isobutylene production form acetone proceeded in accordance with the reaction scheme shown in Fig. 1, indicating that the active site for the reaction is acid sites. As the reaction progressed, the conversion drastically decreased shown in Fig. 2, most likely due to coke deposition on the acid sites. Coke deposition on the acid sites reduces the acid strength, causing decreased conversion as reaction time increases. The sequence of reaction steps also largely terminates at the production of isobutylene, thus leading to an apparent increase in the selectivity for olefins. Therefore, the control of the acidity of BEA zeolite is important for increasing the isobutylene yield as well as inhibiting coke formation.

3.2. Selective isobutylene synthesis over alkali metal ion-exchanged BEA zeolites

In order to control the acid strength of BEA zeolite, alkali metal ion-exchanged BEA zeolites were prepared. Fig. 3 shows the NH_3-TPD profiles of H-BEA and the ion-exchanged BEA zeolites. Two desorption peaks are typically observed in the TPD profiles of zeo-

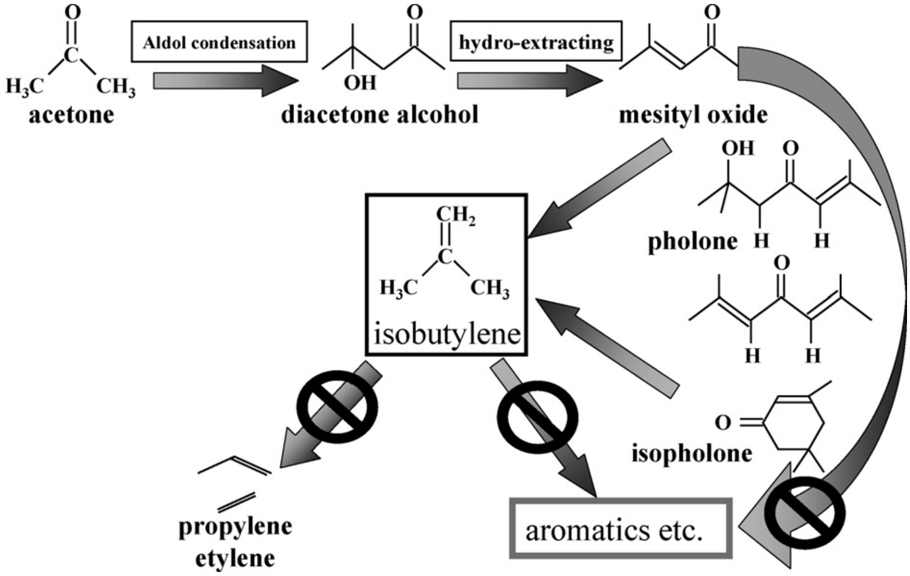

Fig. 1. Reaction route to produce isobutylene from acetone over solid-acid catalyst.

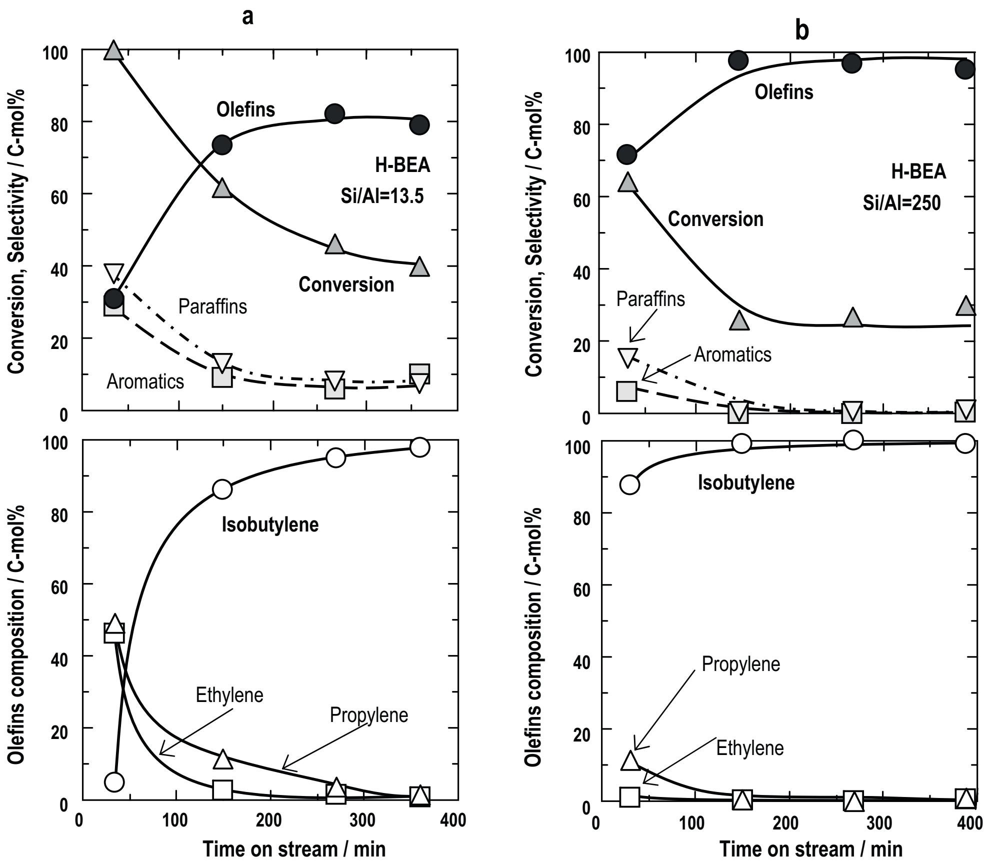

Fig. 2. Changes in acetone conversion, product selectivities and olefins composition with time over H-BEA zeolite with different Si/Al ratio ((a) 13.5 and (b) 250). Reaction temperature and *W*/*F* were 773 K and 0.5 h, respectively.

lites. The peak in the high temperature region is associated with desorption of NH_3 adsorbed on the strong acid sites, whereas the peak in the low temperature region is assigned to NH_3 weakly held by or physically adsorbed on the zeolite. The H-BEA zeolite exhibited two NH_3 desorption peaks, corresponding to strong and weak acid sites.

The molar ratios of Si and alkali metals to Al in alkali metal-exchanged BEA zeolites were listed in Table 1. The Si/Al ratio decreased with ammonium nitrate and alkali metal-exchange treatments due to dealumination. After ion-exchange treatment, although it was considered that the ion-exchange degrees of Na and Cs were insufficient, the desorption peak in the high temperature region above 600 K indicative of strong acid sites effectively decreased and/or disappeared when compared to the H-BEA zeolite.

Isobutylene synthesis from acetone was carried out over the ion-exchanged BEA zeolites. The relationship between acetone conversion and isobutylene selectivity at the initial reaction time of 30 min for the different catalysts can be seen in Fig. 4. The relationship between acetone conversion and isobutylene selectivity at a *W*/*F* of 0.5 h could be plotted on a single curve. The order of catalytic activity was as follows: H-BEA, Na-BEA, K-BEA, Rb-BEA, Cs-BEA, and is the same as the order of acidity of the zeolites shown in Fig. 3. Though the degrees of exchanged alkali metals were different form each catalysts, the acidity affected the catalytic activity because the acetone conversion proceeded on the acid sites of the zeolites. As compared to H-BEA zeolite, the ion-exchanged BEA zeolites exhibited high isobutylene selectivity under high acetone conversion conditions.

The changes in acetone conversion with reaction time are shown in Fig. 5. Although the H-BEA zeolites exhibited the highest

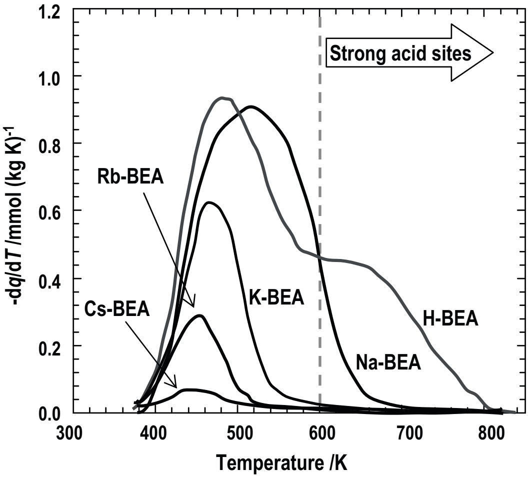

Fig. 3. Changes in the NH_3-TPD profiles of BEA zeolite prior to and after alkali metal ion-exchange treatment.

Table 1
Molar ratios of Si and alkali metals to Al in ion-exchanged BEA zeolites.

Catalyst	Si/Al	(Alkali metal)/Al
Parent BEA	13.5	–
H-BEA	19.3	–
Na-BEA	23.0	0.2
K-BEA	23.9	3.4
Rb-BEA	23.6	1.9
Cs-BEA	21.6	0.5

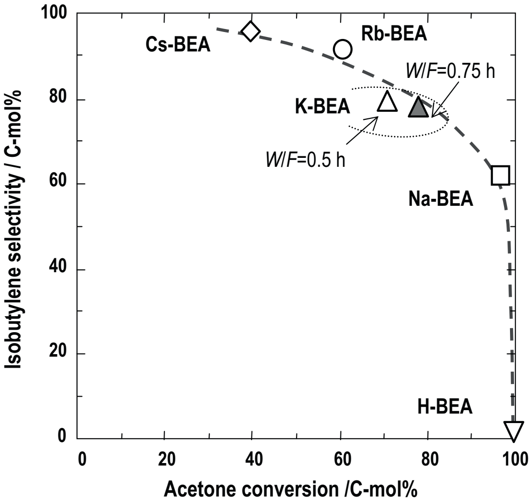

Fig. 4. Relationship between acetone conversion and isobutylene selectivity.

acetone conversion initially, the conversion drastically decreased with increasing reaction time. In contrast, the ion-exchanged BEA zeolites exhibited stable activities throughout the course of the reaction. Because K-BEA exhibited high isobutylene selectivity and acetone conversion, the effects of reaction time and *W*/*F* values for this catalyst were investigated. Changes in acetone conversion and product selectivities with time at *W*/*F* values of 0.5 and 0.75 can be seen in Fig. 6(a) and (b), respectively. As the weight ratio of catalyst to feed acetone (*W*/*F*) increased from 0.5 to 0.75, the acetone conversion increased from approximately 75 to 80% at the initial reaction time of 30 min. Moreover, K-BEA at a *W*/*F* value of 0.75 exhibited both high olefin selectivity and low aromatic production. Less than approximately 10% of aromatics were observed at a *W*/*F* of 0.5 h, and the yield of isobutylene reached approximately 55% at a *W*/*F* of 0.75 h. These results demonstrated that the acidity of BEA zeolite could be controlled using the alkali metal ion-exchange method, resulting in suppressed coke formation, and that the K-BEA zeolite is an effective catalyst for selective production of isobutylene.

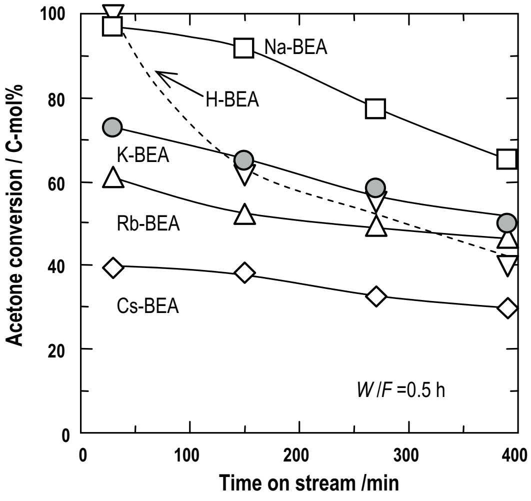

Fig. 5. Changes in acetone conversion with time over H-BEA and alkali metal ion-exchanged BEA zeolites. Reaction temperature and *W*/*F* were 773 K and 0.5 h, respectively.

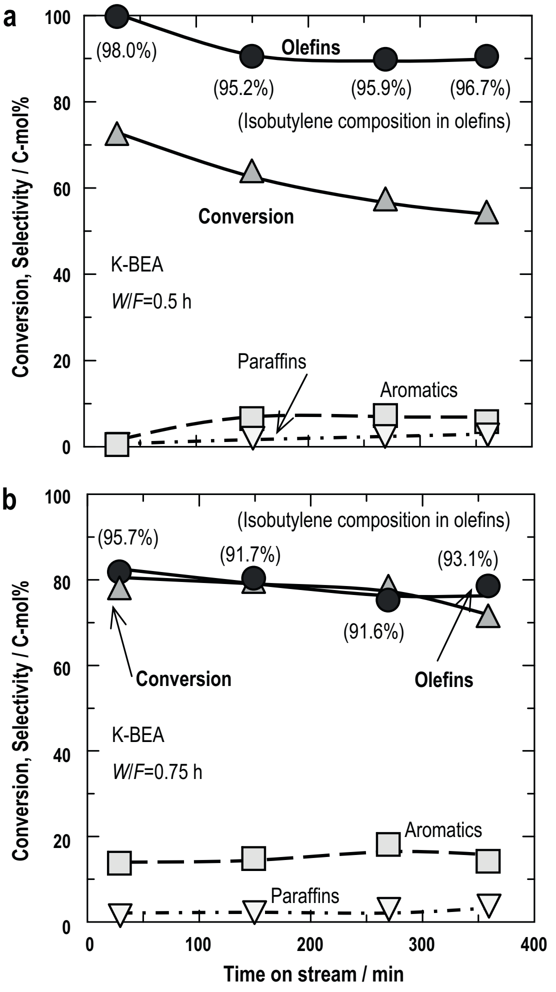

Fig. 6. Changes in acetone conversion and products selectivity with time over K-BEA zeolites with different *W*/*F* values ((a) *W*/*F* = 0.5 and (b) *W*/*F* = 0.75 h). Reaction temperature was 773 K, and values in parentheses in both figures indicate the percent of isobutylene in the olefins produced.

3.3. Amount of coke on the catalysts

Because the acetone conversion proceeded on the acid sites of the zeolites, the acidity of zeolites affected aromatic production and coke formation. Based on the fact that the ion-exchanged BEA zeolites showed decreased production of aromatics compared to H-BEA zeolite, it was expected that coke formation was also reduced with these catalysts. To confirm this theory, the amount of coke formed on the catalysts after reaction for 6 h was measured by thermogravimetric analysis. Fig. 7 shows the changes in catalyst weights during calcination under an oxygen–nitrogen mixture flow (oxygen concentration of 10%). Though approximately 53 wt% of coke was formed on H-BEA, the coke deposited on the alkali metal ion-exchanged BEA zeolites was less than 10 wt%. With the H-BEA zeolite, further reaction of isobutylene occurred over the strong acid sites, resulting in formation of aromatics and coke, and leading to a short lifetime for the catalyst, as shown in Fig. 5. In contrast, further reaction of isobutylene to form aromatics was mostly inhibited, when using the alkali metal ion-exchanged BEA zeolites, which thus lead to inhibition of coke formation. Moreover, onset temperatures for coke combustion with the ion-exchanged BEA zeolites were lower than that of H-BEA zeolite. Because the alkali metal ions have an affinity to oxygen, it was considered that the adsorbed oxygen on alkali metal accelerated coke burning.

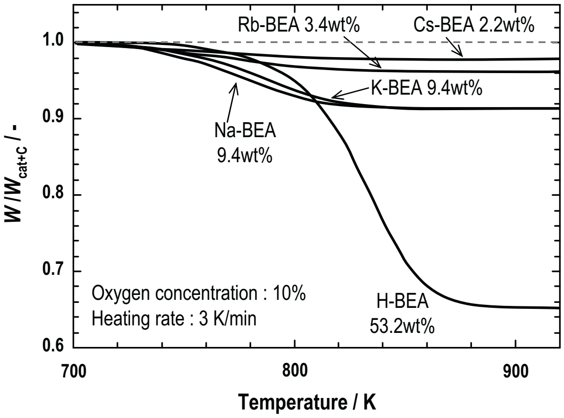

Fig. 7. Changes in catalyst weight during thermogravimetric analysis. The catalysts samples were collected after being used for acetone conversion for 6 h.

4. Conclusions

Selective synthesis of isobutylene was examined using H-BEA and alkali metal ion-exchanged BEA zeolites as catalysts. The acidity of the zeolites, which affected the catalytic activity as well as the isobutylene selectivity, could be controlled using the ion-exchanged treatment. Because the strong acid sites in the ion-exchanged BEA zeolites were mostly eliminated, undesired reactions that produce aromatics were inhibited, leading to an increase in the isobutylene yield and the depression of coke formation on the catalysts. K-BEA zeolite exhibited the highest isobutylene yield at approximately 55%.

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