1. Introduction

Isobutane alkylation with 1-butene is an effective process for production of gasoline components with the highest octane rating, called alkylate. Alkylate is one of the products that can avoid stricter environmental regulations for gasoline because of its low saturated vapor pressure, and low sulfur, aromatic and unsaturated hydrocarbon contents. Commercially, only hydrofluoric acid (HF) and concentrated sulfuric acid (H2SO4) are used as catalysts1). These liquid catalysts present challenges in use such as toxicity, corrosion, and pollution. Therefore, solid acid processes are under active investigation to solve these problems2)–4). The major problem for alkylation on solid acid catalysts is rapid deactivation of the catalyst. In general, only zeolites with large pores show promising activity for alkylation, but rapid deactivation is caused by carbon deposition on the acid site1),5),6). In this process, hydride transfer is the most important reaction because this reaction can prevent carbon deposition on zeolites by suppressing multi-alkylation and oligomerization. Therefore, the rate of hydride transfer should be faster than that of multi-alkylation or oligomerization of 1-butene7),8). The continuously stirred tank reactor (CSTR) has been identified as a suitable process for alkylation using solid acid catalyst because this system can maintain a lower 1-butene concentration, in which oligomerization of 1-butene can be suppressed9),10). Recently, we investigated the activity and stability for alkylation of isobutane with 1-butene in a CSTR, based on the catalytic nature of H-β zeolite. Various preparation methods for H-β zeolite were investigated to optimize the catalytic activity for alkylation, including Si/Al ratio, H+ /Na+ ion exchange rate, and grain size of zeolite. The relationship between Brønsted acid amount and butene consumption over the catalyst lifetime showed a positive correlation. H-β zeolite with larger grain size and prepared with longer crystallization time achieved higher alkylate yield based on the higher hydride transfer activity.

2. Experimental

2.1. Catalysts Preparation

H-β zeolites were prepared by the DGC method or a hydrothermal synthesis (HTS) method. Tables 1 and 2 show typical gel compositions and crystallization conditions. A catalyst prepared by the DGC method was denoted as “DGC,” and a catalyst prepared by the HTS method as “HTS.” The number after “DGC” shows the SiO2/Al2O3 ratio of each gel composition, and the number after “HTS” shows the SiO2/Al2O3 ratio of each gel composition. Colloidal silica (30.7 wt%, Na2O 0.43 wt%, Nissan Chemical Industries, Ltd.), NaAlO2 (Al2O3 36.5 wt%, Na2O 33.0 wt%, Kanto Chemical Industry Co., Ltd., prepared to be SiO2/Al2O3 = 20, 25, 30 or 40), NaOH (97.0 %, Kanto Chemical Industry Co., Ltd.) and
TEAOH (20 wt% solution, Aldrich) were used as reagents. For the DGC method, these reagents were mixed and aged at room temperature for 2 h, and the obtained gel was dried at 353 K with stirring. The dried gel was crystallized in a 100 mL autoclave with 1.8 mL of distilled water at 448 K for 24 h. After washing, the obtained solid was dried at 383 K overnight, then calcined at 813 K for 8 h under 100 mL min\(^{-1}\) of air to obtain Na\(^–\)BEA zeolite. Na\(^–\)BEA zeolite was mixed with 1 N (1 N = 0.5 mol) NH\(_4\)NO\(_3\) (Kanto Chemical Industry Co., Ltd.) solution containing 40 times the amount of \(\text{NH}_4^+\) cation to Al amount. Soaked Na\(^–\)BEA was kept at 353 K for 1 h and washed with distilled water after cooling. These operations were repeated 3 times, then the solid dried at 383 K overnight to obtain NH\(_4\)-(Na\(^–\))BEA zeolite. The sample was calcined at 813 K for 8 h under 100 mL min\(^{-1}\) of air to obtain H\(^–\)(Na\(^–\))BEA zeolite.

2.2. Catalyst Characterization

Zeolite structures were determined by powder X-ray diffraction (XRD, RINT-2100, Rigaku Corp.) using Cu \(K\alpha\) radiation. All crystalline structures of prepared samples were identified as *BEA zeolite. Acid amounts were measured by NH\(_3\)-TPD (temperature programmed desorption of ammonia, BEL-CAT, BEL Japan Inc.). The sample was pretreated with He flow for 1 h at 773 K. After drying, NH\(_3\) adsorption was conducted at 373 K for 30 min. The sample was then heated at a rate of 10 K min\(^{-1}\) up to 883 K, and the desorbed NH\(_3\) concentration was recorded by a thermal conductivity detector (TCD).

Infrared measurements of adsorbed pyridine were performed on all samples using FT-IR (Fourier Transform Infrared spectroscopy, IR Prestige-21, J. Jpn. Petrol. Inst., Vol. 56, No. 5, 2013).

| Catalyst               | Acid amount [mmol g\(^{-1}\)] | Brønsted acid amount [mmol g\(^{-1}\)] | Lewis acid amount [mmol g\(^{-1}\)] | B/(B + L) [-] |
|------------------------|-------------------------------|----------------------------------------|------------------------------------|---------------|
| DGC-HB20               | 0.72                          | 0.52                                   | 0.20                               | 0.72          |
| DGC-HB25               | 0.78                          | 0.64                                   | 0.14                               | 0.82          |
| DGC-HB30               | 0.64                          | 0.55                                   | 0.08                               | 0.87          |
| DGC-HB40               | 0.56                          | 0.44                                   | 0.12                               | 0.79          |
| DGC-HB25 (NaOH treatment) | 0.75                         | 0.45                                   | 0.30                               | 0.60          |
| DGC-HB25 75 % H\(^+\)  | 0.73                          | 0.61                                   | 0.12                               | 0.84          |
| DGC-HB25 50 % H\(^+\)  | 0.61                          | 0.51                                   | 0.10                               | 0.83          |

Each sample was crystallized for 24 h at 448 K.

| Catalyst               | Acid amount [mmol g\(^{-1}\)] | Brønsted acid amount [mmol g\(^{-1}\)] | Lewis acid amount [mmol g\(^{-1}\)] | B/(B + L) [-] |
|------------------------|-------------------------------|----------------------------------------|------------------------------------|---------------|
| HTS-7d-600             | 0.62                          | 0.50                                   | 0.12                               | 0.81          |
| HTS-7d-800             | 0.61                          | 0.40                                   | 0.20                               | 0.67          |
| HTS-7d-1000            | 0.54                          | 0.36                                   | 0.18                               | 0.67          |
| HTS-14d-450            | 0.88                          | 0.81                                   | 0.07                               | 0.92          |
| HTS-14d-600            | 0.75                          | 0.60                                   | 0.15                               | 0.80          |
| HTS-14d-800            | 0.70                          | 0.58                                   | 0.11                               | 0.84          |
| HTS-14d-1000           | 0.66                          | 0.56                                   | 0.10                               | 0.85          |
| HTS-14d-1400           | 0.56                          | 0.36                                   | 0.20                               | 0.64          |
| HTS-28d-600            | 0.86                          | 0.69                                   | 0.18                               | 0.80          |
| HTS-28d-800            | 0.73                          | 0.59                                   | 0.14                               | 0.81          |
| HTS-28d-1000           | 0.70                          | 0.54                                   | 0.15                               | 0.78          |

Gel composition was 30.0 Si\(_2\)O\(_5\) : 1.0 Al\(_2\)O\(_3\) : 3.0 Na\(_2\)O : 11.1 TEAOH : \(\chi\) H\(_2\)O (molar ratio; \(\chi\) is 450, 600, 800, 1000 or 1400), crystallization was conducted at 413 K.
Shimadzu Corp.) to determine the Brønsted/Lewis acid site ratio. The sample was pretreated in vacuo for 1 h at 773 K. Then, pyridine vapor was introduced into the cell and kept at 373 K for 10 min. The cell was evacuated at 523 K for 30 min to eliminate physisorbed pyridine, and the remaining pyridine was measured by FT-IR at 373 K. Correction coefficient by Emeis\(^{(3)}\) was used to determine the Brønsted/Lewis acid site ratio.

Scanning electron micrography was recorded using a FE-SEM (field emission scanning electron microscope, S-4800, Hitachi, Ltd.) to measure the grain size of the H-\(^{+}\)-BEA zeolites. The Si/Al ratio of the DGC-H-\(^{+}\)-BEA zeolite was determined by ICP (inductively coupled plasma, SPECTRO-CIRO-CCD, Rigaku Corp.). The BET specific surface area of the DGC-H-\(^{+}\)-BEA zeolite was measured by nitrogen adsorption (BELSORP mini, BEL Japan Inc.) at 77 K.

### 2. 3. Catalytic Experiments

The catalytic reaction was performed in a CSTR (continuous stirred tank reactor) with 30 mL volume\(^{11,12}\). Reaction conditions were as follows; temperature 363 K, pressure 2.0 MPa, and stirring rate 780 rpm. As a pretreatment, H-\(^{+}\)-BEA zeolite catalyst, which was sieved to a grain size of 355-710 \(\mu\)m, was heated at a rate of 3 K min\(^{-1}\) to 773 K under air flow for 2 h. The catalyst was charged into the reactor under \(N_2\) gas. Then, the reactor was filled with liquefied isobutane and was heated at 363 K with stirring. After the preset temperature was observed, feedstock (isobutane/1-butene = 30) was introduced into the reactor using a high-pressure syringe pump (500D; ISCO Corp.). Total flow rate of the feedstock was 0.46 or 0.69 mL min\(^{-1}\) to 773 K under air flow for 2 h. The catalyst was charged into the reactor under \(N_2\) gas. Then, the reactor was filled with liquefied isobutane and was heated at 363 K with stirring. After the preset temperature was observed, feedstock (isobutane/1-butene = 30) was introduced into the reactor using a high-pressure syringe pump (500D; ISCO Corp.). Total flow rate of the feedstock was 0.46 or 0.69 mL min\(^{-1}\) to 773 K under air flow for 2 h. The catalyst was charged into the reactor under \(N_2\) gas. Then, the reactor was filled with liquefied isobutane and was heated at 363 K with stirring. After the preset temperature was observed, feedstock (isobutane/1-butene = 30) was introduced into the reactor using a high-pressure syringe pump (500D; ISCO Corp.). Total flow rate of the feedstock was 0.46 or 0.69 mL min\(^{-1}\) to 773 K under air flow for 2 h. The catalyst was charged into the reactor under \(N_2\) gas.

### 3. Results and Discussion

#### 3. 1. Characterization of Zeolites

Table 1 shows the physicochemical properties of DGC-H-\(^{+}\)-BEA zeolites. DGC-HB crystallized with lower SiO\(_2\)/Al\(_2\)O\(_3\) ratio gel composition tended to have higher acid content in the DGC-HB series (DGC-HB20, 25, 30, 40), because of the increasing Al content in H-\(^{+}\)-BEA zeolite. DGC-HB25 treated with NaOH solution had lower B/(B + L) ratio than the parent DGC-HB25, because of the erosion of Si into the NaOH solution, collapsing zeolite structure, and formation of octahedrally coordinated Al within the extra framework as a Lewis acid site. In the series of DGC-HB25 with different H\(^{+}\)/Na\(^{+}\) ion exchange rates, DGC-HB25 mixed with higher NH\(_4\)\(^{+}\) concentration solution tended to have higher acid content.

Table 2 shows the physicochemical properties of HTS-H-\(^{+}\)-BEA zeolites. HTS-H-\(^{+}\)-BEA crystallized with gel composition of lower H\(_2\)O/Al\(_2\)O\(_3\) ratio tended to have higher acid content and B/(B + L) ratio among the HTS-H-\(^{+}\)-BEA zeolites despite the same crystallization time, because Al cations are incorporated more easily into the framework of zeolite under such conditions. Longer crystallization time results in more regularly structured zeolite framework.

Figure 1 shows the scanning electron micrographs of DGC and HTS-H-\(^{+}\)-BEA. HTS-H-\(^{+}\)-BEA zeolites crystallized with higher H\(_2\)O/Al\(_2\)O\(_3\) ratio gel tended to have larger grain size, because nuclear growth occurred preferentially to nuclear deposition.

#### 3. 2. Catalytic Activities of Various Zeolites

Table 3 shows the alkylation characteristics of various DGC H-\(^{+}\)-BEA zeolites and Fig. 2(a) shows the yields of the products and the selectivity for 2,2,4-trimethylpentane over DGC-HB25 catalyst, which showed the highest activity and the longest lifetime among DGC-H-\(^{+}\)-BEA zeolites. The maximum yield of C\(_8\) paraffin was 120-150 % (maximum value is 200 % based on 1-butene). The alkylate was selectively produced over these H-\(^{+}\)-BEA zeolites, and 1-butene was not detected during the lifetime. Although activity/stability was maintained during the lifetime in all tests, the yield of C\(_8\) paraffin and conversion of 1-butene decreased after the lifetime. These catalysts had the following lifetime order: DGC-HB40 < DGC-HB20 = DGC-HB25 (NaOH treatment) < DGC-HB30 < DGC-HB25. As shown in our previous studies\(^{11,12}\), deactivation of H-\(^{+}\)-BEA zeolite is caused by pore plugging with higher hydrocarbons. The formation of n-butane occurs via hydride transfer between n-butyl cation and isobutane. As shown in Fig. 2(a), the yield of C\(_5\)-C\(_7\) increased up to a stable value, then decreased with lower yield of C\(_8\) paraffin. C\(_5\)-C\(_7\) hydrocarbons were formed by the cracking of C\(_8\) or higher hydrocarbons because no formation of C\(_1\)-C\(_3\) hydrocarbons was detected. Table 3 also shows the selectivity for 2,2,4-TMP was around 50 % and for 2,3,4-TMP was about 20 %. 2,3,3,-TMP and dimethylhexane were
formed in only small amounts. As previously reported\textsuperscript{11,12}, these selectivities for C\textsubscript{8} alkylate were typical for alkylation using H\textsuperscript{+}-BEA zeolites.

3.3. Effect of Ion Exchange Rate

Next, the alkylation reaction was investigated over DGC-HB25 zeolites with different ion exchange rates between H\textsuperscript{+} and Na\textsuperscript{+}; 100 \% H\textsuperscript{+}, 75 \% H\textsuperscript{+} (i.e. 25 \% Na\textsuperscript{+}), and 50 \% H\textsuperscript{+} (i.e. 50 \% Na\textsuperscript{+}), using reaction temperature 363 K, OSV 0.48 g\textsubscript{butene} g\textsubscript{catalyst} h\textsuperscript{-1}, and paraffin/olefin ratio 30. Figure 3 shows the alkylation performances over these H\textsuperscript{+}-BEA zeolites. The lifetime order was as follows: DGC-50 \% H\textsuperscript{+} < DGC-75 \% H\textsuperscript{+} < DGC-100 \% H\textsuperscript{+}, probably due to difference in Brønsted acid amount. Moreover, this observation suggested that H\textsuperscript{+}/Na\textsuperscript{+} ratio (i.e. Brønsted acid amount) was an important factor for determining the lifetime of the catalyst.

3.4. Effect of the Grain Size

To elucidate the effect of grain size of zeolite, alkylation reaction was performed with the HTS-H\textsuperscript{+}-BEA series with different grain diameters, using reaction temperature 363 K, OSV 0.48 g\textsubscript{butene} g\textsubscript{catalyst} h\textsuperscript{-1}, and paraffin/olefin ratio 30. The HTS method can easily control the grain size of the H\textsuperscript{+}-BEA zeolite by changing the H\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} ratio. Table 4 shows the alkylation performance over the HTS-H\textsuperscript{+}-BEA series. The lifetime order was as follows: HTS-7d-1000 < HTS-7d-600 < HTS-14d-1400 < HTS-14d-450 < HTS-28d-1000 = HTS-28d-600. The yield of n-butane, an indicator for the hydride transfer activity, was approximately 25 \% over HTS-7d-1000, HTS-28d-1000, and HTS-14d-1400 at reaction time 30 min. In contrast, yield of n-butane was approximately 15 \% over HTS-14d-450, HTS-7d-600, and HTS-28d-600. These findings suggested that H\textsuperscript{+}-BEA crystallized from higher H\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} ratio composition gel had higher hydride transfer activity, possibly due to the higher grain size of H\textsuperscript{+}-BEA. In general, the ratio of acid sites in pores to that at the outer surface increases with larger grain size. Inner pore acid sites might have higher hydride transfer activity. C\textsubscript{8} paraffin yield showed more stable activity during the lifetime over HTS-28d-1000 than over other zeolites. This phenomenon might depend on the difference in the acid amount ratio and the feedstock diffusion rate between

![Scanning Electron Micrographs of (a) HTS-14d-450, (b) HTS-7d-600, (c) HTS-28d-600, (d) HTS-7d-1000, (e) HTS-28d-1000, (f) HTS-14d-1400, (g) DGC-HB25](image)

Table 3  Alkylation Performances over Various DGC-H\textsuperscript{+}-BEA Catalysts

| Catalyst     | Lifetime [h] | Yield [%] | Selectivity for 2,2,4-trimethylpentane [%] |
|--------------|--------------|-----------|------------------------------------------|
|              | n-butane | butene | C\textsubscript{5}-C\textsubscript{7} | C\textsubscript{8} alkylate |                      |
| DGC-HB20     | initial   | 13.9    | 0.0    | 17.1    | 140.5    | 48.3                      |
| DGC-HB25     | initial   | 6.7     | 4.8    | 23.7    | 87.8    | 44.4                      |
| DGC-HB30     | initial   | 12.7    | 0.0    | 15.6    | 137.2   | 50.2                      |
| DGC-HB40     | initial   | 4.5     | 4.6    | 21.5    | 68.9    | 43.0                      |
| DGC-HB25 (NaOH treatment) | 4.0 | 11.5 | 0.0 | 16.2 | 135.0 | 49.4 |
| DGC-HB25 (75 \% H\textsuperscript{+}) | initial | 1.5 | 5.2 | 2.8 | 25.5 | 82.4 | 44.2 |
| DGC-HB25 (50 \% H\textsuperscript{+}) | initial | 1.5 | 7.7 | 0.8 | 11.7 | 106.9 | 49.5 |

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the inner pore and the outer surface of the zeolite. Among these zeolites, HTS-28d-1000 showed the best performance for C8 alkylate production, and had higher inner pore Brønsted acid amount which might have high hydride transfer activity. Consequently, the hydride transfer and alkylation reaction rate for C8 production were higher.

Figure 4 shows the relationship between total butene consumption and total acid amount, Brønsted acid amount or Lewis acid amount in the zeolite catalyst. Butene consumption and total acid amount or Brønsted acid amount showed positive correlation. Therefore, Brønsted acid amount affects the catalyst lifetime in the alkylation of isobutane by 1-butene using H-\(^+\)BEA zeolite. From these results, H-\(^+\)BEA with lower SiO\(_2\)/Al\(_2\)O\(_3\) ratio had less pore plugging and longer lifetime than catalysts with higher SiO\(_2\)/Al\(_2\)O\(_3\) ratio, and larger grain size resulted in higher hydride transfer activity.
4. Conclusion

The relationship between acid amount or Brønsted acid amount and butene consumption showed a positive correlation for alkylation of isobutane by 1-butene over H-BEA zeolite in CSTR. Lower SiO$_2$/Al$_2$O$_3$ ratio of H-*BEA resulted in longer lifetime, and a ratio around 25 was suitable for long life catalyst. H-*BEA crystallized with higher H$_2$O/Al$_2$O$_3$ ratio gel composition had larger grain size, which resulted in higher inner pore Brønsted acid site amount. Optimized synthesis conditions enabled higher performance for C$_8$ alkylate production resulting from the higher hydride transfer activity.
References

1) Feller, A., Zuazo, I., Guzman, A., Barth, J. O., Lercher, J. A., J. Catal., 216, 313 (2003).
2) Weitkamp, J., Traa, Y., Catal. Today, 49, 193 (1999).
3) Blasco, T., Corma, A., Martinez, A., Martinez-Escolano, P., J. Catal., 177, 306 (1998).
4) Clark, M. C., Subramaniam, B., Ind. Eng. Chem. Res., 37, 1243 (1998).
5) Nivarthy, G. S., Feller, A., Seshan, K., Lercher, J. A., Microporous Mesoporous Mater., 35-36, 75 (2000).
6) Mota Salinas, A. L., Sapaly, G., Ben Taarit, Y., Vedrine, J. C., Appl. Catal. A: General, 336, 61 (2008).
7) Simpson, M. F., Wei, J., Sundaresan, S., Ind. Eng. Chem. Res., 35, 3861 (1996).
8) Corma, A., Martinez, A., Martinez, C., Catal. Lett., 28, 187 (1994).
9) Feller, A., Guzman, A., Zuazo, I., Lercher, J. A., J. Catal., 224, 80 (2004).
10) Lyon, C. J., Sarsani, V. R., Subramaniam, B., Ind. Eng. Chem. Res., 43, 4809 (2004).
11) Sekine, Y., Ichikawa, Y., Tajima, Y., Nakabayashi, K., Matsukata, M., Kikuchi, E., J. Jpn. Petrol. Inst., 55, (5), 299 (2012).
12) Sekine, Y., Tajima, Y., Ichikawa, Y., Matsukata, M., Kikuchi, E., J. Jpn. Petrol. Inst., 55, (5), 308 (2012).
13) Emeis, C. A., J. Catal., 141, 347 (1993).

要 旨
H-ベータゼオライトを用いた CSTR 中でのイソブタンの1-ブテンによるアルキル化（第3報）
H-ベータゼオライトの酸特性の反応への影響

加藤 優基，藤岡 慎也，中林 啓太，市川 洋介，菊地 英一，関根 奉
早稲田大学先端理工学部応用化学科，169-8555 東京都新宿区大久保3-4-1

イソブタンのアルキル化反応は高オクタン値のアルキレートガソリンを製造する上で重要な反応である。これまでに我々は、CSTR を用いた1-ブテンによるイソブタンのアルキレーションにおいて、DGC 法で調製したベータ型ゼオライトが他のゼオライトに比べて高い活性・安定性を示すことを見出した。この触媒は酸量と B/(B+L) 比率が高い値を示した。様々な方法で H-ベータゼオライトを合成し、アルキル化のための最適な因子としてケイ素アルミニウム比率やカチオン交換比率、ゼオライト2次粒子径依存性などを検討した。プレンステッド酸量と劣化までのブテン消費量には正の相関がみられた。さらに、2次粒子径の大きな H-ベータゼオライトはより高い性能を示した。

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