Catalytic isomerization of n-hexane over beta (BEA) zeolite by dry-gel convention (DGC) and hydrothermal (HTS) methods

Pusparatu¹* and Y Sugi²

¹ Politeknik Energi dan Mineral Akamigas, Blora, Indonesia
² Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Japan

*Email: pusparatu@esdm.go.id

Abstract. Catalytic Isomerization of n-hexane over Beta (BEA) zeolite synthesized by dry gel conversion (DGC) and hydrothermal (HTS) methods were studied. The isomerization was influenced by types of synthesized methods, and combined selectivity for branched alkanes (2- and 3-methylpentanes, 2,2-dimethylbutane, 2, and 3-methylbutanes, 2,2-dimethylpropane, and 2-methylpropane) decreased in the order: BEA (DGC) > BEA (HTS). BEA synthesized by DGC had the highest activity and selectivity for the isomerization, and BEA Synthesized by HTS has the highest activity for cracking to lower alkanes and alkenes. These differences are ascribed to the difference of surface area, pore volume, acid properties, and reaction parameters.

1. Introduction

Acid catalysed transformations of hydrocarbons are important processes in petroleum refining processes such as reforming, isomerization, alkylation, cracking, etc. In particular, catalytic isomerization and cracking of alkanes play important roles in fuel and chemical production, because it provides branched alkanes and lower olefins [1]. Many workers have attention to find effective catalysts for the isomerization of alkanes over solid acid catalysts such as zeolites [2,3], noble metal loaded zeolites [4], zirconia sulphate [5], and MoO₃ [6].

There are many researches on the isomerization and the cracking of normal alkanes over zeolites. BEA, MWW, FAU, MFI, etc. [7-10]. The isomerization and the cracking have the similar character and related reaction mechanism: they are influenced by many factors, such as acidic properties, pore structures, and particle sizes. It has been reported that BEA and MWW are the most efficient catalysts for the isomerization [11], and MFI is the highly active for the cracking [12]. BEA has a three-dimensional intersecting channel system: two mutually perpendicular straight channels, each with a cross section of 0.76 x 0.64 nm, run in the a- and b-directions. A sinusoidal channel of 0.55 x 0.55 runs parallel to the c-direction [13]. MFI has three-dimensional intersecting channels system. A straight channel of 0.56 x 0.53 nm runs parallel to the a-axis and a-sinusoidal channel of 0.55 x 0.51 nm runs parallel to the b-axis [14]. MWW has two independent pores system [15]. One is defined by two-dimensional sinusoidal channels, which assessable by 10- rim apertures. The other consists of large elongated super cages of 0.71 x 1.82 nm. These differences of pore structure of BEA and MFI derive the differences of catalytic features.

Dry-gel conversion (DGC) method is a synthetic technique using dry gel without bulk aqueous phase. Two different but interrelated methods are proposed for DGC method: vapour-phase transport (VPT, as...
used by Kim et al. [16]) and steam-assisted conversion (SAC, as used by Matsukata et al. [17]) methods. The particle size obtained by these methods is usually smaller than conventional hydrothermal synthesis methods. DGC method has many merits for environmental conscious synthesis for molecular sieves: the method involves minimization of waste disposal and reduction in reactor volume, and allows nearly complete conversion of gel to high crystalline molecular sieves with high yield. Uniform crystals with small particle size were obtained by this technique. In this paper, we studied the effects of methods preparation of BEA zeolite on the isomerization of n-hexane.

2. Experimental

2.1. Synthesis of zeolites

Synthesis of BEA by DGC method [18]. A typical procedure (100 mmol of SiO$_2$) was as follows: 15.57 g (37 mmol) of TEAOH solution (35 wt%) was mixed with 1.14 g (7.2 mmol) of a 25.2 wt% aqueous solution of NaOH, followed by the addition of 15.02 g colloidal silica (Ludox HS-40 (40 wt%), containing 6.01 g (100 mmol) of SiO$_2$, and the mixture was stirred for 30 min. 0.34 g (0.01 mmol) of Al$_2$(SO$_4$)$_3$ was dissolved in 30.63 ml of warm water and added to the above mixture. The molar composition was: SiO$_2$:0.37TEAOH:0.072NaOH:0.01Al$_2$O$_3$:17H$_2$O. Resultant mixture was stirred for further 2 h at room temperature, and then, the gel was dried for ca. 5 h on an oil bath at 80-90°C with continuous stirring. The dried and powdered gel was transferred to a Teflon cup (55 mm x 37 mm I.D.). This cup was placed in a Teflon-lined autoclave (125 ml) with the support of a Teflon holder. A small amounts of external bulk water (ca. 0.2 g per 1 g of dry gel) was added in Teflon cup, and it was placed at the bottom of the autoclave. The crystallization was carried out at 175°C for 30 h. After the crystallization was completed, the autoclave was cooled to room temperature. The zeolite was removed from the cup, washed thoroughly with distillate water and dried at room temperature overnight. The results of synthesis are summarized in Table 1.

![Table 1. Gel composition, synthesis condition, and products for BEA by HTS.](image)

| Exp. No. | SiO$_2$ | Al$_2$O$_3$ | NaOH | SDA | Temp. (°C) | Time (d/h) | Phase |
|---------|---------|-------------|------|-----|------------|------------|-------|
| 1       | 1       | 0.02        | 0.3  | 0.35$^a$+ 1$^b$ | 20         | 150        | 7d    | BEA  |
| 2       | 1       | 0.02        | 0.3  | 0.35$^a$+ 0.5$^b$ | 20         | 150        | 7d    | BEA+ MFI |
| 3       | 1       | 0.033       | 0.3  | 0.5$^a$ | 20         | 150        | 6h    | BEA  |
| 4       | 1       | 0.033       | 0.3  | 0.5$^a$ | 20         | 150        | 12h   | BEA  |
| 5       | 1       | 0.033       | 0.3  | 0.5$^a$ | 20         | 150        | 24h   | BEA  |
| 6       | 1       | 0.033       | 0.3  | 0.5$^a$ | 20         | 150        | 3d    | BEA  |
| 7       | 1       | 0.033       | 0.3  | 0.5$^a$ | 20         | 150        | 5d    | BEA  |
| 8       | 1       | 0.033       | 0.3  | 0.5$^a$ | 20         | 150        | 7d    | BEA  |
| 9       | 1       | 0.009       | 0.3  | 0.5$^a$ | 20         | 150        | 7d    | BEA  |
| 10      | 1       | 0.01        | 0.3  | 0.5$^a$ | 20         | 150        | 7d    | BEA  |
| 11      | 1       | 0.015       | 0.3  | 0.5$^a$ | 20         | 150        | 7d    | BEA  |
| 12      | 1       | 0.02        | 0.3  | 0.5$^a$ | 20         | 150        | 7d    | BEA  |
| 13      | 1       | 0.025       | 0.3  | 0.5$^a$ | 20         | 150        | 7d    | BEA  |
| 14      | 1       | 0.03        | 0.3  | 0.5$^a$ | 20         | 150        | 7d    | BEA  |
| 15      | 1       | 0.04        | 0.3  | 0.5$^a$ | 20         | 150        | 7d    | BEA  |

$^a$ = tetraethylammonium bromium (TEABr)  
$^b$ = tetraethylbromium hydroxide (TEAOH)

Synthesis of BEA by HTS method. High SiO$_2$/Al$_2$O$_3$ ratio of BEA can be synthesized by HTS using tetra ammonium bromide (TEABr) and TEAOH as the SDAs according to the literature [19]. Typical procedure for synthesis of [Al]-BEA by hydrothermal method in high SiO$_2$/Al$_2$O$_3$ region was as follows: 18.93 g (45 mmol) of TEAOH (Aldrich, 35 wt% aqueous solution), 18.91 g (90 mmol) of TEABr (Aldrich) followed by 0.276 g (3 mmol) of NaAlO$_2$ (33.7 wt% Al$_2$O$_3$, 42.8 wt% Na$_2$O) were taken in a Teflon jar and stirred for about 10 min. To the above alkaline solution, 22.53 g (150 mmol) of Ludox...
HS 40 (40 wt% of colloidal SiO$_2$) was added, and this solution was stirred for another 10 min. Finally, 5.024 g (33 mmol) triethanolamine was added and the gel was stirred for 3 h. This gel was then transferred into a 125 ml Teflon-lined autoclave and 0.045 g (0.5 wt% of SiO$_2$) of [Al]-BEA (previously prepared without seed) as seeds were added. The autoclave was heated at 150°C for 180 h. The gel composition of the sample is listed in Table 1. The solid obtained was filtered, washed with distilled water, and dried overnight. The sample was calcined in air (100 ml/min) at 550°C for 10 h.

To remove the organic SDA occluded inside the pores, the as-synthesized zeolite sample was kept in a muffle furnace, and heated in a flow of air (50 ml/min). The temperature was increased from room temperature to 550°C for 4 h (2°C/min), and maintained at this temperature for 7 h. Finally, the sample was cooled to room temperature under ambient conditions.

2.2. Catalytic experiments
Catalytic isomerization and cracking of hexane were carried out using a 9 mm (OD) quartz tubular down flow reactor. The zeolite (1 g; 18/32 meshes) was placed between two layers quartz wool, and heated in a stream of 20 ml/min of nitrogen at 550°C for 1 h. before introducing hexane. The reaction was performed at temperature at 350-650°C. The products were analysed with on-line gas chromatographs using fused silica capillary columns with FID detector. The capillary columns are CP-Al$_2$O$_3$/KCl (HP, 50 m x 0.53 mm, 10 μm film thickness) for the analysis of C$_1$-C$_6$ hydrocarbons, and HR-1 column (GL Sciences, Tokyo, Japan) for C$_7^+$ hydrocarbons, benzene, toluene, and xylenes.

3. Result and Discussion

3.1. Properties of BEA synthesized by DGC and HTS
The SiO$_2$/Al$_2$O$_3$ ratios of synthesized BEA in this study were summarized in Table 1. DGC method gave BEA with the different SiO$_2$/Al$_2$O$_3$ ratio (33 – 203) from the similar ratios in gel composition. However, HTS method by literature using TEAOH as SDA [27] gave BEA with the range of SiO$_2$/Al$_2$O$_3$ ratio from 17-33, if the gel composition was changed from 25 to 110 as shown in Figure 1. BEA (100) with SiO$_2$/Al$_2$O$_3$ ratio =100 was obtained using mixtures of TEAOH and TEABr as SDA in the presence of triethanolamine under the hydrothermal conditions [20].

Figure 1 shows the SEM images of typical BEA used as catalysts in this study. The crystal size of BEA synthesized by DGC method is smaller than that of BEA synthesized by HTS method. It is clear that small crystal size of BEA can be synthesized by DGC method.

![BEA(30)_HTS](image1)
![BEA(30)_DGC](image2)
![BEA(100)_HTS](image3)
![BEA(100)_DGC](image4)

**Figure 1.** SEM images of BEA by DGC and HTS methods

Table 2 summarizes the properties of BEA zeolite used as the references in this study. The values of specific surface area by BET method, pore volume and external surface area by t-plot method were almost comparable by both DGC and HTS methods.
| Zeolite      | Si/Al2 Ratio\(a\) | Diameter Dimension (nm) | BET SA\(c\) (m\(^2\)/g) | N2- Desorption | External SA\(c\) (m\(^2\)/g) | Total SA\(f\) (m\(^2\)/g) | Acid amount (mmol/g) | Temp (\(^0\)C) |
|-------------|------------------|--------------------------|-----------------------------|----------------|-------------------------------|-------------------------|----------------------|-----------------|
| BEA(DGC)   | 33               | 0,76 3                   | 471                         | 108            | 168                           | 644                     | 0,310                | 300             |
| BEA(DGC)   | 102              | 0,76 3                   | 530                         | 122            | 167                           | 748                     | 0,140                | 300             |
| BEA(HTS)   | 21               | 0,76 3                   | 580                         | 133            | 182                           | 831                     | 0,424                | 300             |
| BEA(HTS)   | 160              | 0,76 3                   | 682                         | 157            | 109                           | 998                     | 0,178                | 300             |

\(a\) = measured by ICP; \(b\) = referents; \(c\), \(d\) = BET methods; \(e\), \(f\) = t plot method

Figure 2 also shows NH\(_3\)-TPD profiles of BEA with different SiO\(_2\)/Al\(_2\)O\(_3\) ratio. Two desorption peaks are recognized in all BEA samples, low temperature peak is assigned as desorption of physically adsorbed NH\(_3\), and high temperature peak is corresponding to Bronsted acidity. High temperature peaks of all BEA samples are almost the same temperature at around 300\(^0\)C, and the acid amounts presented as peak height is proportional to SiO\(_2\)/Al\(_2\)O\(_3\) ratio of BEA zeolites. These results indicate that BEA zeolites have very similar acidic properties, even changing the SiO\(_2\)/Al\(_2\)O\(_3\) ratio. Furthermore, the deference of synthesis methods, DGC and HTS, is not observed in acidic character.

Si- and Al- MASNMR spectra are shown in Fig. 3. Clear AlO-Si (O-Si)\(_3\) peaks assigned as framework tetrahedral aluminium were observed with Si(O-Si)\(_4\) peaks in all BEA. Al-MASNMR of BEA (30) by the DGC and HTS methods show the existence of very small amount of extra-framework aluminium. However, aluminium in frameworks was only observed for BEA (100) by both DGC and HTS methods.
3.2. The isomerization over BEA
Table 3. shows the typical results in the isomerization of hexane over BEA synthesized by DGC and HTS methods. The conversions of hexane over these BEAs were in almost the same level at early stages, and the deactivation of catalytic activity occurred over all BEA zeolites: the deactivation rate of BEA synthesized by HTS is higher than those of BEA by DGC. The difference of activity deterioration between two catalysts is due to their difference of coke deposition: coke deposition of BEA by DGC is less than that of BEA by HTS during the reaction. The catalytic features of all zeolites were quite resembled to each other’s except coke formation phenomena. The reasons of coke formation difference by synthetic methods are not clear yet; however, the low coke formation during reaction is one of good feature for the catalysis. From these observations, we chose BEA by DGC for the detail studies.

| Method Preparation | DGC | HTS |
|--------------------|-----|-----|
| SiO₂/Al₂O₃ Ratio   | 33  | 103 |
| Conversion (% wt)  | 14.4| 13.7|
| Branched Paraffin (% wt) | 65.6| 69.3|
| 2-Methylpropana    | 19.3| 24.6|
| 2-Methylbutana     | 11.2| 14.0|
| 3-Methylpentana    | 22.2| 8.3 |
| 2,3-Dimethylbutana | 1.6 | 1.8 |
| 2,2-Dimethylbutana | 0.2 | 0.2 |
| Conversion b       | 11.9| 11.1|
| Coke deposition b  | 6.5 | 3.1 |

a Reaction Conditions: Catalyst 1g ; feed hexane 2.29 mmol/min ; Carrier gas (N₂) 0.89 mmol/min ; w/f 8.17 g h/mol. Data were taken after 1 h reaction
b Data were taken 260 min the reaction started

4. Conclusion
Isomerization and cracking of alkanes to branched alkanes was studied over BEA zeolites. Catalytic activity and selectivity are influenced by surface area, pore volume, acidic properties, and reaction parameters. BEA has the weak acid sites to enhance the isomerization and to prevent deep cracking, and wide pore structure easily to diffuse isomerization products. Each acid site on all BEA works as uniform and discrete catalytic site for the isomerization, judging from their catalysis and NH₃-TPD.

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