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Zeolite Beta by Dry Gel Conversion (DGC) Method: An Efficient Catalyst for the Isomerization of Hexane

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Isomerization and cracking of hexane were studied over several types of zeolites: Beta (BEA), ZSM-22 (MWW), ZSM-5 (MFI), and mordenite (MOR). The isomerization was influenced by types of zeolite, and the selectivity for branched alkanes (2- and 3-methylpentanes, 2,2-dimethylbutane, 2- and 3-methyl butanes, 2,2-dimethylpropane, and 2-methylpropane) decreased in the order: BEA > MWW > MFI. BEA has the highest activity and selectivity for the isomerization, and MFI has the highest activity and selectivity for cracking to lower alkanes and alkenes. These differences are ascribed to the difference of pore-structure, acid properties, and reaction parameters. Effects of SiO_2/Al_2O_3 ratio by dry gel conversion (DGC) method were examined in the isomerization of hexane. Combined selectivity for branched alkanes was in the similar level, however, selectivity of branched C5 and C4 products decreased with the increase of the ratio. The selectivity for the isomerization was not influenced by the amount of acid sites, and the cracking of the isomerization products was enhanced by acid amounts. Catalytic activity and selectivity for branched alkanes was in the similar level. These results suggest that each acid site on all BEA has uniform and discrete activity with selectivity for the isomerization, and support the conclusion that the acidity of BEA has weak and uniform from NH_3-TPD measurements.

Keywords: isomerization, cracking, hexane, branched alkane, zeolite; BEA

1. INTRODUCTION

Catalytic isomerization and cracking of alkane plays important roles in petroleum industry, because it provides branched alkanes and lower olefins [1]. Now days, the isomerization of normal alkanes is important for supply of high octane fuels to gasoline pool. 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 sulfate [5], and MoO_3 [6]. Recently, BEA found as a candidate with high activity and selectivity for the isomerization [4]. In this paper, we describe isomerization and cracking of hexane over Beta (BEA) by DGC method to discuss their catalytic properties, and compare with other types of zeolites: ZSM-22 (MWW), ZSM-5 (MFI), and mordenite (MOR).

2. EXPERIMENTAL

2.1 Catalyst preparation

BEA(30), BEA(60), BEA(100), BEA(200), MFI(39), MWW(20) and MOR(30) were as H^+-form used as catalysts. (Values in parenthesis are SiO_2/Al_2O_3 ratios.)

BEA was synthesized by DGC method [7]. 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_2O_3:17H_2O. The resultant mixture was stirred further for 2 h, 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. Small amounts of external bulk water (*ca.* 0.2 g per 1 g of dry gel), 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 over night. 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 up to 550 °C for 4 h (2 °C/min), and maintained at this temperature for 7 h. Finally, the zeolite sample was cooled to room temperature.

MWW was synthesized hydrothermally according to previous literature [8]. As-synthesized samples were calcined at 550°C for 7 h. Proton form was obtained by refluxing with ammonium nitrate solution, and calcined at 550°C for 7 h.

MFI was supplied from Tosoh as ammonium form (HSZ-840NHA), and changed to H-form by calcination. MOR was obtained from Tosoh as H-form (Tosoh; HSZ-670HOA).

2.2. Characterization of catalysts

Powder X-ray diffraction was measured by Shimadzu XRD-6000 with Cu Kα radiation (λ =1.5418 Å). Elemental analysis was performed using inductive coupled plasma atomic emission spectroscope (JICP-

PS-1000 UV Leeman Labs Inc). Scanning electron microscopy (SEM) was recorded using a Philips XL30 microscope. Nitrogen adsorption measurements were carried out on a Belsorp 28SA (Bel Japan). Ammonia temperature programmed desorption (NH_3-TPD) was measured using a TPD-66 apparatus (Bel Japan): the catalyst was evacuated at 400 °C for 1h, and ammonia was adsorbed at 100 °C followed by further evacuation for 1h. Then, the sample was heated from 100 to 710 °C at the rate of 10 °C/min in a helium stream. TG analysis was performed on Shimadzu TG-DTG-50 analyzer with temperature-programmed rate of 10 °C/min in an air stream.

2.3. 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 analyzed with on-line gas chromatographs using fused silica capillary columns with FID detector. The capillary columns are CP-Al_2O_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) C_7^+ hydrocarbons, benzene, toluene, and xylenes.

The conversion of hexane and the selectivity for the products were calculated on carbon basis:

$$\text{Fed hexane (mol/min)} = \sum_i \text{Area}_i \times C_i \times F_i/N_i$$

$$\text{Conversion} = \frac{(\text{Fed hexane} - \text{Area}_o \times C_o \times F_o/N_o)}{\text{Total amount}} \times 100$$

$$\text{Yield}_i \text{ of each component} = \frac{(\text{Area}_i \times C_i \times F_i/N_i)}{\text{Fed hexane}} \times 100$$

$$\text{Selectivity of each component} = \text{Yield}_i / \text{Conversion}$$

Area_i = GC area of each component

Area_o = GC area of hexane

In this paper, methylpentanes (2- and 3-methylpentanes and 2,2-dimethylbutane), methylbutanes (2- and 3-methylbutanes and 2,2-dimethylpropane), and 2-methylpropane were abbreviated as **b-C6**, **b-C5**, and **b-C4**, respectively. Combined selectivity for the isomerization is sum of **b-C6**, **b-C5**, and **b-C4.**

3. RESULTS AND DISCUSSION

3.1. Properties of zeolites

Table 1 shows typical properties of zeolite in this study. SiO_2/Al_2O_3 ratios were in the range of 20-40. Surface area was in the order: BEA >> MWW, MOR, MFI. XRD shows these zeolites have high crystallinity.

NH_3-TPD profiles of the H^+-form of BEA, MWW, MFI and MOR are shown in Fig.1a. There are two stages of NH_3 desorption with peak maxima at around 160 °C and 300 °C in all zeolites. The first peak (peak 1) appeared at around 160 °C is ascribed to the desorption of physisorbed NH_3. The second peak (peak 2) higher than 300 °C is due to the desorption of NH_3 from Brønsted and Lewis acid sites. The peak temperature and area is indicator of acid properties such as acid strength and amounts. Peak temperature increased in the order: BEA < MFI < MWW << MOR. This order shows BEA has weaker acid strength than the others. Total acid amounts calculating from area in Fig. 1 are 0.31, 0.16, 0.34 and 0.38 mmol/g for BEA, MWW, MFI and MOR, respectively.

Table 1. Properties of zeolites

Zeolite	SiO_2/Al_2O_3	Pore diameter (nm)	Dimension	Surface area (m^2/g)	NH_3-TPD temperature (°C)
BEA	30	0.76	3	530	300
MWW	20	0.82	3	382	340
MFI	39	0.55	3	370	380
MOR	31	0.67	1	377	450

Figure 1b shows NH_3-TPD of BEA with different SiO_2/Al_2O_3 ratio. All BEA zeolites have the peak at around 300 °C which are due to Brønsted acidity. They have the almost same peak temperature for all BEA, and acid amounts are proportional to SiO_2/A_2O_3 ratio. These result shows that the acidity of BEA by DGC method is uniform and independent from the ratios.

3.2. Catalytic cracking by zeolites

Figure 2 shows the time on stream on isomerization and cracking of hexane over zeolites. Catalytic activity decreased in the order: MFI > BEA > MWW >> MOR. MFI have the highest activity, however, cracking to lower alkenes was predominant. BEA had high activity and selectivity for the isomerization, although some deactivation occurred during the reaction. MWW and MOR had lower activity for the conversion. Particularly, MOR had rapidly lost the activity. These differences are due to the difference in coke-deposition. Coke-deposition on large pore zeolites, such as BEA and MOR, occurs at intra and external surfaces, but it is limited only on external surface on MFI [9]. This means that catalytic activity of MFI is not easily deactivated by coke-deposition. However, the coke-deposition occurs in one-dimensional channel of MOR to lose rapidly its catalytic activity; however, the deactivation of BEA occurs only gradually by coke-deposition in their three

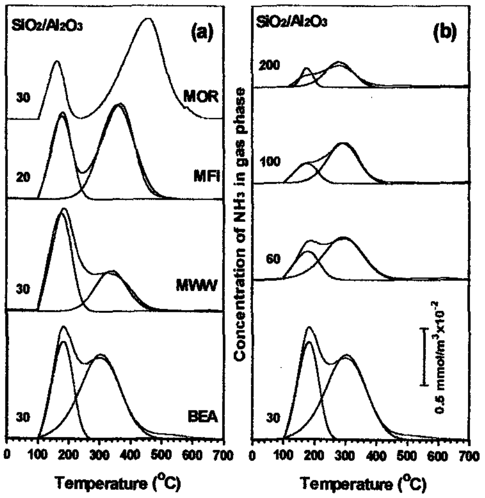

Fig. 1. NH_3-TPD profiles of (a) typical zeolites and (b) BEA with different SiO_2/Al_2O_3 ratio

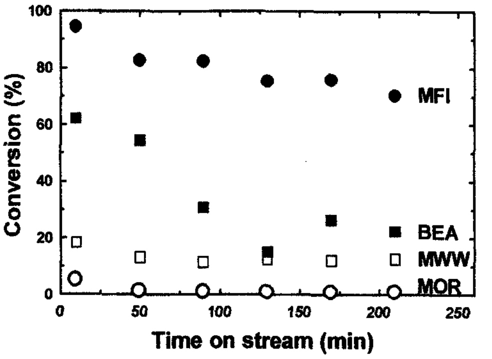

Fig. 2. Effects of time on stream on catalytic activity over zeolites. Reaction conditions: temperature, 350°C; fed hexane, 2.29 mmol/min; carrier gas (N_2), 0.89 mmol/min, W/F, 8.17 g.h/mol.

dimensional pores.

The selectivity for the isomerization (combined selectivity for branched alkanes) at the initial stages was BEA > MWW >> MFI as also shown in Fig. 3a. BEA has the highest activity and selectivity for the isomerization, and the cracking is enhanced over MFI. However, there is a possibility that the selectivity depends on the conversion; it is necessary to compare the selectivity at the same level of the conversion to discuss their catalytic behaviors. Fig. 3b shows selectivity for isomerization at *ca.* 13 % of hexane conversion over BEA, MWW, and MFI. Data were taken after 60 min from starting by adjusting W/F. The selectivity for branched alkanes decreased in the order, BEA > MWW >> MFI: these catalytic features are very similar to the results at the initial stages. These results show that BEA has the highest potential for the isomerization of hexane.

It is considered that branched hexanes (2- and 3-methylpentanes and 2,2-dimethylbutane) are formed via the isomerization also *via* carbenium cation intermediate. The selectivity for the isomerization is influenced by the factors, such as structure of zeolite, acid strength and amounts, and by reaction parameters [10]. However, some characteristic features from our results are as follows. First, the cracking decreased with the decrease of pore mouth of zeolites. Narrow pores of zeolite enhance cracking in the order: BEA < MWW < MFI, and suggest that the diffusion of the products is one of factors for the cracking. Furthermore, the increase of 2-methylbutane, 2,2-dimethylpropane, and 2-methylpropane, which were yielded by β-scission at tertiary carbenium ion, increased in the same order. This trend suggests that cracking of isomerized products enhanced in MFI pore by limited diffusion. However, pore structure of BEA enhances the diffusion of isomerization products before they crack to lower branched alkenes inside pores. Secondly, acid strength is related to isomerization and cracking. The selectivity for isomerization was the highest for BEA, which has the weakest acid strength, and zeolite with strong acidity such as MFI should enhance cracking to reduce the selectivity for the isomerization.

3.3. Catalysis by BEA

BEA has the highest selectivity for the isomerization and uniform acidity as shown in previous section. To elucidate high catalytic performances of BEA, we studied the effects of SiO_2/Al_2O_3 ratio on the isomerization of hexane.

3.3.1. Effects of temperature. Figure 4 shows the effects of reaction temperature on the selectivity for branched alkanes in cracking and isomerization of hexane. The isomerization was predominant at lower temperature. The cracking enhanced with the increase of temperature, and the selectivity for the isomerization is only less than 10 % at 640 °C.

The isomerization to branched alkanes occurs via carbenium ion [11]. Carbenium ion is formed at C_2 or C_3 carbon on acid sites of the zeolite, and methyl cation rearranges to branched cation, and release of H^+ resulted in the formation of branched alkanes. The resultant branched alkanes are higher reactivity for further isomerization to multi-branched alkanes. The branched alkanes are more reactive than normal alkanes because

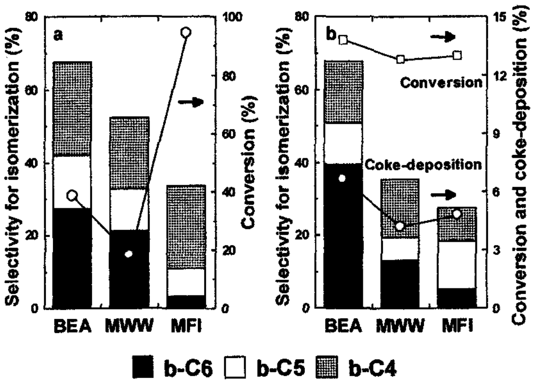

Fig. 3. The isomerization of hexane over zeolites (a) at the selectivity in the initial stage and (b) in the similar conversion level. Reaction conditions temperature 350 °C (a) fed hexane, 2.29 mmol/min; N_2, 0.89 mmol/min, W/F=8.17 g.h/mol. Data was taken after 20 min from starting. (b) W/F, 8.17 (BEA), 0.52 (MFI), 8.17 (MWW) g.h/mol. Data: Conversion and selectivity: after 60 min from starting. coke deposition 260 min on stream.

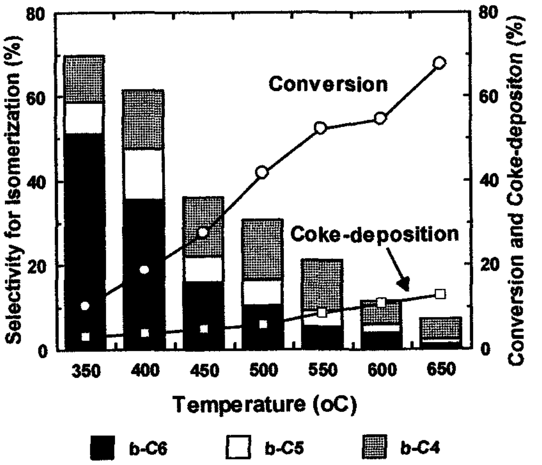

Fig. 4. Effect of reaction temperature on the selectivity for the isomerization. Reaction condition: feed of hexane, 2.29 mmol/min; carrier gas (N_2), 0.89 mmol/min; W/F, 8.17 g.h/mol. Data in Fig.: Conversion and selectivity for branched alkanes: taken at 60 min from starting. coke deposition: 260 min on stream.

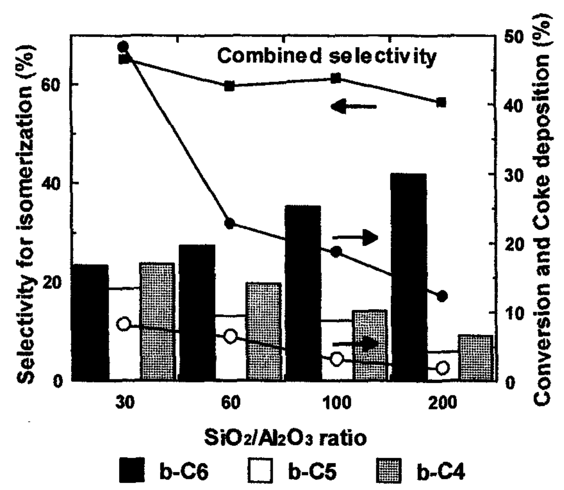

Fig. 5. Effects of SiO_2/Al_2O_3 ratio of BEA on the selectivity for the isomerization. Reaction conditions: temperature, 400 °C; fed hexane, 2.29 mmol/min, carrier gas (N_2), 0.89 mmol/min; W/F, 8.17 g.h/mol. Data: Conversion and selectivity: 60 min from starting; Coke deposition: 260 min on stream.

of easier formation of carbenium ion. The resultant cation will give lower alkanes by β-scission. As discussed above, BEA has the highest selectivity for the isomerization. Enhancement of the isomerization by BEA suggests that strong acidity is not necessary for the isomerization because strong acid sites such in MFI catalyze the deep cracking. The pore structure of BEA is one of the reasons for high selectivity for the isomerization. MFI could also promote the isomerization, but the cracking is much enhanced because of low diffusivity of the isomerization products in its pore and of their higher reactivity for the cracking.

3.3.2. Effect of SiO_2/Al_2O_3 ratio. We examined the effects of SiO_2/Al_2O_3 ratio of BEA on the isomerization of hexane. The activity decreased with the increase of the ratio as shown in Fig. 6. However, the combined selectivity of branched alkanes was in the similar level for all BEA. The selectivity for **b-C6** increased with the increase of Al_2O_3/SiO_2 ratio, however, the selectivity for cracked isomerization products, **b-C4** and **b-C5**, decreased in the reverse order. These results suggest that selectivity for the isomerization does not influence by the amount of acid sites, and the cracking of the isomerization products enhances by acid amounts.

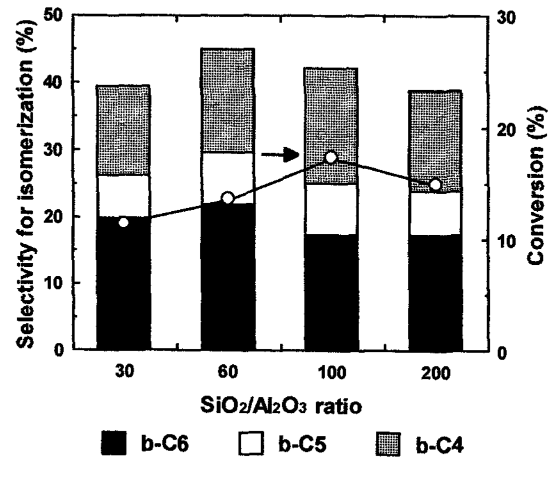

Fig. 6. Effects of SiO_2/Al_2O_3 ratio of BEA on the selectivity for the isomerization normalized with aluminum amounts. Reaction conditions: temperature, 400°C; fed hexane, 0.15 ml/min (1.15 mmol); carrier gas (N_2) 20 ml/min (0.89 mmol); W/F, 1.23, 2.45, 4.09, 8.17 (g·h/mol). Data were taken after 1 h from starting.

In order to confirm how the amount of acid sites is influenced to the catalysis, we examined the comparison of catalytic performances with normalized with amount of acid sites by changing W/F. Fig. 6 shows the effect of Al_2O_3/SiO_2 ratio normalized with aluminum amounts. The selectivity on branched alkanes was in the similar levels for the isomerization by all BEA. These results mean that each acid site on all BEA has uniform and discrete activity with selectivity for the isomerization, support the conclusion that the acidity of BEA has weak and uniform from NH_3-TPD measurements.

4. CONCLUSIONS

Isomerization and cracking of alkanes to branched alkanes was studied over zeolites. Catalytic activity and selectivity are influenced by pore structures, acidic properties, and reaction parameters. BEA has the highest activity and selectivity for the isomerization of hexane among zeolites. 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 NH_3-TPD.

Further investigation on noble metal modification of the BEA is under progress.

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