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Dehydrogenation and Isomerization of Butane over Cr Catalysts Supported on H-SSZ-35 Type Zeolites

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The dehydrogenation and isomerization of butane to isobutene over Cr catalysts supported on zeolites were investigated. Although a zeolite support, especially with a low Si/Al_2 ratio, favors the cracking of butane over its dehydrogenation and isomerization, due to strong solid acidity, the loading of Cr on a zeolite support enhances the dehydrogenation and isomerization of butane. H-SSZ-35 type zeolite, which has a one-dimensional cage-type channel structure, was hydrothermally synthesized using *cis*,*cis*,*cis*-*N*-methylhexahydrojulolidinium hydroxide as a structure-directing agent (SDA). We found that Cr/H-SSZ-35 ($Si/Al_2 = 500$) showed moderate butane conversion and isobutene selectivity. As a result, the yield of isobutene (conversion of butane × selectivity of isobutene) was the highest among the catalysts used in this study. Its activity at 500 °C remained unchanged for 6 h. Our evidence suggests that butane was dehydrogenated over the zeolite support or Cr_2O_3 particles, and a proportion of the dehydrogenated products were isomerized to isobutene over the zeolite support.

Isobutene is an important intermediate for many common petrochemicals and plastics, and in order to synthesize isobutene, the dehydrogenation of isobutane[1–3] and the skeletal isomerization of butenes[4–6] had been studied quite extensively. For the dehydrogenation of isobutane, it has been reported that Cr oxide-based catalysts are effective. For example, Hoang et al. studied the dehydrogenation of isobutane over Cr_2O_3 supported on various rare earth materials (Cr_2O_3 supported on $La_2(CO_3)_3$, $Sm_2(CO_3)_3$, and $Pr_2(CO_3)_3$).[1] Rossi et al. used CrO_x/ZrO_2, CrO_x/γ-Al_2O_3, and CrO_x/SiO_2,[2] and Grzybowska et al. also used CrO_x/γ-Al_2O_3.[3]

On the other hand, in the skeletal isomerization of butene, the solid acidity of catalysts plays an important role. Gielgens et al. have reported on the skeletal isomerization of 1-butene over WO_3/γ-Al_2O_3 catalysts.[4] Houzvicka et al. have studied the skeletal isomerization of butene to isobutene over an open-surface catalysts and several ZSM-5 samples, and found that the weak acidity of catalysts (H_3PO_4/SiO_2 and H-[Fe]-ZSM-5) favored the high selectivity of isobutene.[5] Seo et al. have investigated reversible skeletal isomerization between butenes and isobutene, and found that FER, F/Al_2O_3, and KIT-1 showed a high selectivity of isobutene from butenes and butenes from isobutene.[6]

However, when using these methods, two processes (dehydrogenation and skeletal isomerization) are still required to obtain isobutene from butane, and, from the standpoint of energy saving, the simultaneous dehydrogenation and isomerization of butane to isobutene is highly desirable. Wang et al. have reported on the simultaneous dehydrogenation and isomerization of butane to isobutene over Cr-based ZrO_2 catalysts under oxidative conditions[7] and Cr-based WO_3-promoted catalysts under non-oxidative conditions.[8] In these studies, it was found that Cr/WO_3–ZrO_2 had the highest activity of dehydrogenation and isomerization of butane to isobutene under both oxidative and non-oxidative conditions. Kishida et al. investigated the direct conversion of butane to isobutene over metal oxide catalysts supported on γ-alumina, and found that, of various kinds of metal oxides, Ga(III) oxide catalyst alone could convert butane to isobutene; and doping of Cu(II) to the Ga(III) oxide catalyst led to the highest yield of isobutene.[9]

Kishida et al. have also found Pt catalysts to be more effective for the direct conversion of butane to isobutene than Ga(III) catalysts supported on corresponding zeolite-like materials, and that Pt catalyst supported on MFI-type silicoferrate(III) produced isobutene at the highest yield.[10] On the other hand, Byggningsbacka et al. have reported on the combination of Zn-modified K-ZSM-5 with a ZSM-22 system for the simultaneous dehydrogenation and isomerization of butane to isobutene.[11] In their report, butene was obtained over a Zn-modified K-ZSM-5 dehydrogenation catalyst, and isobutene was obtained from butene over a ZSM-22 skeletal isomerization catalyst. Pirngruber et al. studied the dehydrogenation and isomerization of butane over Pt-ZSM-5 catalysts with a high Si/Al ratio, and found that the highest yield of isobutene was approximately 12.5% at 830 K and 1.8 bar, and with a feed of 10% butane and 20% hydrogen.[12]

On the other hand, zeolites have micropores with ordered size and solid acidity and, as mentioned above, there has been growing interest in applications of zeolites as catalysts as well as molecular sieves. We have investigated the synthesis of novel zeolites using ammonium salts as structure-directing agents (SDAs).[13,14] SSZ-35 has an unusual one-dimensional straight channel structure with pore openings that alternate between rings of ten tetrahedral atoms (10MR) and eighteen tetrahedral

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atoms (18MR); and the micropore volume of this zeolite is larger than those of other one-dimensional high-silica zeolites. Wagner et al. reported the hydrothermal synthesis of SSZ-35, in which cyclic and polycyclic quaternized amine molecules were used as SDAs.[15,16]

In this study, referring to Wang's reports,[7,8] Cr catalysts were prepared, and the conversion of butane over Cr catalysts was investigated. Moreover, other kinds of metal catalysts were prepared, and the catalytic activity of these catalysts for the conversion of butane was compared with Cr catalysts. As a result, Cr catalysts supported on zeolites, especially H-SSZ-35 ($Si/Al_2 = 500$), were found to be effective for this reaction, and their effects on the conversion of butane and selectivity of products were investigated.

Experimental

Synthesis of Zeolite Support. H-SSZ-35 support was hydrothermally synthesized using *cis*,*cis*,*cis*-*N*-methylhexahydrojulolidinium hydroxide as SDA. The procedure for synthesizing the SDA is shown in Fig. 1. *cis*,*cis*,*cis*-*N*-Methylhexahydrojulolidinium hydroxide was synthesized as follows: 2,6-bis(2-cyanoethyl)cyclohexanone was obtained from cyclohexanone (Wako Pure Chemical) and acrylonitrile (Wako Pure Chemical) as the starting materials, followed by cyclization under a high-pressure hydrogen atmosphere (hydrogen pressure 10 MPa, temperature approx. 120 °C) in an autoclave in the presence of a Raney nickel catalyst, to produce hexahydrojulolidine.[17] The obtained transparent hexahydrojulolidine oil was a mixture of *cis*,*cis*,*cis*-type (used as a precursor of SDA), *cis*,*trans*,*cis*-type, and *cis*,*cis*,*trans*-type. To remove the *cis*,*trans*,*cis*-type and *cis*,*cis*,*trans*-type, hexahydrojulolidine oil was diluted with ether, refluxed with methyl iodide, and cooled. After removing precipitated solids by filtration and evaporating the residual solution, a *cis*,*cis*,*cis*-type transparent oil was obtained. This oil was diluted with toluene and stirred at room temperature. Methyl iodide was then added and the mixture refluxed. After cooling, filtrating and drying, *cis*,*cis*,*cis*-*N*-methylhexahydrojulolidinium iodide, in the form of a white powder, was obtained. It was then converted to hydroxide by ion-exchange resin.

The solution of *cis*,*cis*,*cis*-*N*-methylhexahydrojulolidinium hydroxide was mixed with NaOH (Wako Pure Chemical), colloidal silica (Shokubai Kasei, Cataloid), sodium aluminate (Wako Pure Chemical), and distilled water in a glass beaker, and stirred overnight at room temperature. The ratios were as follows: $Si/Al_2 =$ 40, 100, 500, 1000, $H_2O/Si = 50$, $OH^-/Si = 0.1$, $SDA/Si = 0.2$. Afterwards, the mixture was poured into Teflon-lined autoclaves (Parr Instruments), and the sealed autoclaves were heated at 170 °C for 7 days. The obtained solid of Na-SSZ-35 was filtrated, washed with water and dried. Na-SSZ-35 was calcined at 550 °C for 6 h in air, and converted to NH_4-SSZ-35 by stirring overnight in an ammonium nitrate solution, followed by filtration and drying. The obtained NH_4-SSZ-35 was calcined under the same conditions as those mentioned above to produce H-SSZ-35.

An H-ZSM-12 support was hydrothermally synthesized with hexamethylenebis(triethylammonium hydroxide) ($Et_3N^+(CH_2)_6$-N^+Et_3 $(OH^-)_2$) as SDA.[14] Hexamethylenebis(triethylammonium bromide) was prepared by refluxing 1,6-dibromohexane (Tokyo Kasei) and triethylamine (Tokyo Kasei) in acetone. The precipitated bromide was filtered out, air-dried, and purified by recrystallization using mixed solvents of ethanol and diethyl ether. The recrystallized diammonium salt was air-dried after filtration, followed by conversion to hydroxide using an ion-exchange resin. The solution of hexamethylenebis(triethylammonium hydroxide) was mixed in a Teflon-lined autoclave (Parr Instruments) with colloidal silica (Shokubai Kasei, Cataloid), aluminum nitrate nonahydrate (Kanto Chemical), NaOH (Nakarai Chemicals), and sulfuric acid to adjust the total amount of OH^-. The ratios were as follows: $Si/Al_2 = 200$, 1000, $H_2O/Si = 60$, $OH^-/Si = 0.2$, $Na^+/Si = 0.3$, $SDA/Si = 0.05$. The as-synthesized crystals of Na-ZSM-12 were obtained by heating in a sealed autoclave at 160 °C for 4 days, followed by cooling, washing with distilled water, filtrating, and drying. Na-ZSM-12 was calcined at 500 °C for 6 h in air, and converted to NH_4-ZSM-12 by stirring in a solution of ammonium nitrate while heating for several days, followed by filtration and drying. The obtained NH_4-ZSM-12 was calcined under the same conditions as above to finally obtain H-ZSM-12.

Other zeolite supports, such as USY (Ultra Stable Y zeolite), H-Beta, H-ZSM-5, and H-mordenite, were obtained commercially (Tosoh). Before use, these zeolites were also calcined at 500 °C for 6 h in air.

Characterization of Zeolite Supports. To measure the solid acidity of the supports, NH_3-temperature-programmed-desorption (TPD) experiments on zeolite supports were carried out on an NH_3-TPD apparatus (Ohkura Riken, Model ATD700A). TPD profiles were obtained under a vacuum at temperatures varying from 100 to 600 °C at 10 °C/min in the TPD process. Samples were de-

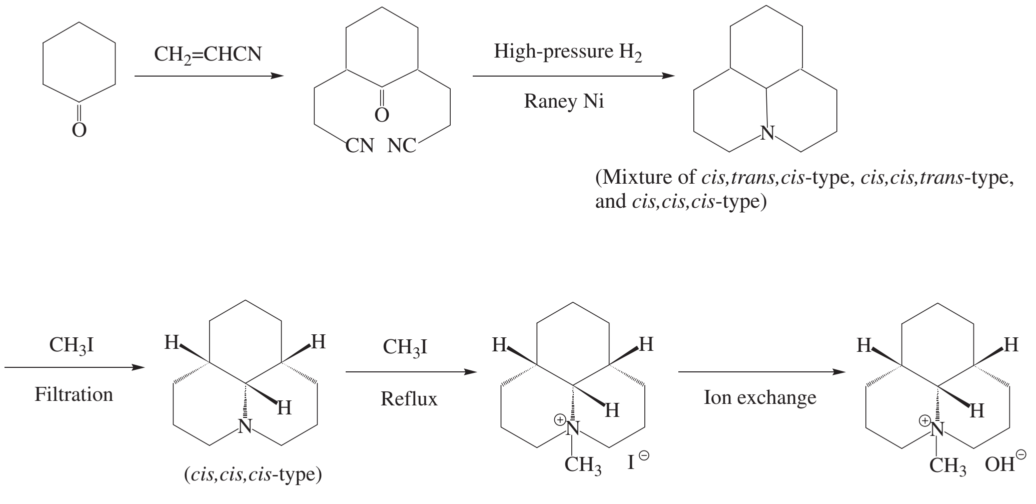

Fig. 1. Synthesis of *cis*,*cis*,*cis*-*N*-methylhexahydrojulolidinium hydroxide.

gassed at 500 °C for 1 h under vacuum conditions before a measurement. The surface area and micropore volume of the zeolite supports were measured by analyzing the adsorption of nitrogen at −196 °C using a volumetric apparatus (Nihon Bel, BELSORP 28SA) after degassing at 300 °C for 5.5 h under a vacuum.

Preparation of Cr Catalysts Supported on Zeolites. Cr catalysts supported on zeolites were prepared by impregnation. As a rule, the loading of Cr was 10 wt %, but in some cases the loading was varied from 5 wt % to 20 wt %. Chromium(III) nitrate nonahydrate (Wako Pure Chemical) was used as the Cr source. After impregnation, the wet catalysts were dried at 100 °C in an oven, followed by calcination at 700 °C for 3 h in air. For a comparison, a Cr catalyst supported on silica was prepared by the same method.

Characterization of Cr Catalysts Supported on Zeolites. Powder X-ray diffraction analysis (Mac Science, M18XHF^{22}-SRA) of Cr-supported catalysts reduced in the flow of hydrogen at 600 °C was performed with Cu Kα radiation, and the diameter of Cr particles was calculated from the line width of XRD patterns.

Measurement of the Catalytic Activity. The catalytic activity was measured using a fixed-bed reactor. The weight of the catalyst was 1 g. Before the reaction, the catalyst was reduced at 600 °C for 2 h in a flow of hydrogen. The effluent gas was analyzed by gas chromatography (GC) with Molecular Sieve 5A and a Porapak Q columns. Two detectors were used: TCD was used to detect hydrogen, and FID to detect hydrocarbons. The reactant gas contained n-C_4H_{10} (20%) and Ar (80%) and the gas flow rate was 60 cm^3 min^{-1}. The reaction temperature was changed from 400 °C to 600 °C in 50 °C steps.

Results and Discussion

Characterization of the Zeolite Support and Cr Catalysts Supported on Zeolites. The XRD pattern of SSZ-35 synthesized in this study is shown in Fig. 2. This pattern is almost the same as the pattern of SSZ-35 (International Zeolite Association Code STF).[15,16] The peaks at about 10° were weaker than those of STF. No impurity peaks were observed.

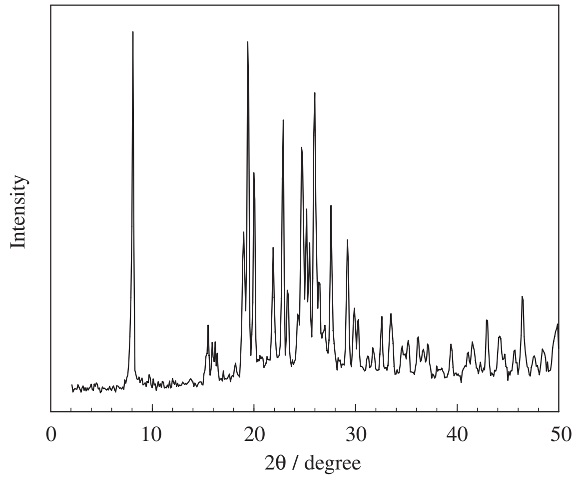

Fig. 2. XRD pattern of SSZ-35 synthesized in this study.

Table 1. Physico-Chemical Properties of H-SSZ-35

Si/Al_2 ratio	Total surface area $m^2\,g^{-1}$	Micropore volume $mm^3\,g^{-1}$	NH_3 adsorption $\mu mol\,g^{-1}$
40	390	172	1010
100	484	214	844
500	486	222	294

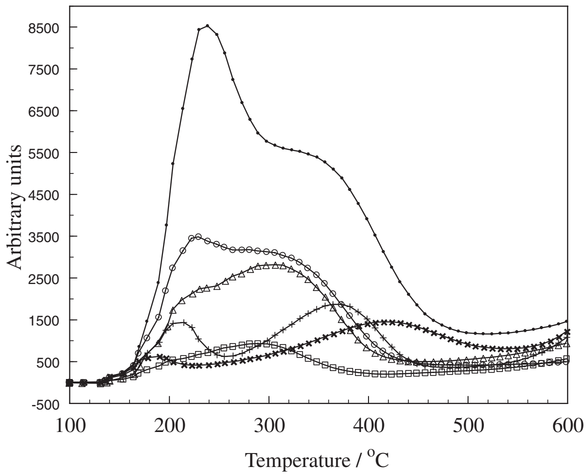

Fig. 3. NH_3-TPD profiles of H-SSZ-35 and other zeolites. (○) H-SSZ-35 ($Si/Al_2 = 40$), (△) H-SSZ-35 ($Si/Al_2 = 100$), (□) H-SSZ-35 ($Si/Al_2 = 500$), (+) H-ZSM-5 ($Si/Al_2 = 190$), (×) H-mordenite ($Si/Al_2 = 240$), (•) H-Beta ($Si/Al_2 = 27$).

Table 1 shows the results of the characterization of H-SSZ-35 ($Si/Al_2 = 40$, 100, 500). An investigation of these results demonstrated that total surface area, and the micropore volume increased with an increased Si/Al_2 ratio, while the NH_3 adsorption decreased with an increased ratio. As shown in Fig. 3, where the NH_3-TPD profile was measured, most zeolites showed two main NH_3 desorption peaks: the desorption peak at higher temperature was caused by solid acid. In the case of H-SSZ-35 type zeolites, desorption peaks at higher temperatures (about 300 °C) were lower than those of other kinds of zeolites, showing that the solid acidity of H-SSZ-35 type zeolites is weaker than that seen in other kinds of zeolites.

An XRD measurement of Cr catalyst supported on zeolite showed that Cr exists as Cr_2O_3 even after reduction in the flow of hydrogen at 600 °C. XRD peaks of Cr_2O_3 appeared at about 24.5, 33.5, 36.2, 41.5, 50.2, and 54.8°, and the size of Cr_2O_3 crystallites calculated from the XRD pattern at 54.8° was about 30 nm, much larger than the diameter of the zeolite micropores. These results indicated that Cr_2O_3 particles were unable to enter the zeolite micropores. There is a possibility that protons in the framework of zeolites are exchanged with Cr cations; however, even if Cr cations exist, it appears that the quantity of Cr cations is negligible, and they do not influence the catalytic activity, since below 5 wt % of Cr-loading, the existence of Cr affected the catalytic activity of Cr-supported catalysts (see Fig. 6). Cr cations may be fully saturated even at low Cr-loading, and do not increase by increasing Cr-loading. From this, it seems that Cr cations do not act as catalytic active sites, but Cr_2O_3 particles do.

Catalytic Activity. Table 2 gives the conversion of butane, the selectivity of each product, and the yield of isobutene over zeolite supports alone and Cr catalysts supported on zeolites at 500 °C. For a comparison, the conversion and selectivity over a silica support and Cr catalysts supported on silica are also shown in Table 2. In most cases, zeolite supports alone were

Table 2. Catalytic Performance of the Various Zeolite Catalysts at 500 °C

Catalyst	Conv.	Selectivity/C-%						Yield of iso-C4′
	C-%	C_{1-3}	Iso -C_4	1 -C_4'	Iso -C_4'	2 -C_4'	1,3 -C_4''	C-%
H-SSZ-35 (40)	50.4	87.1	8.0	0.7	2.0	2.2	0.0	1.01
Cr/H-SSZ-35 (40)	17.1	57.7	18.9	3.8	9.4	10.3	0.0	1.61
H-SSZ-35 (100)	8.6	72.0	4.6	0.0	6.6	9.9	6.9	0.57
Cr/H-SSZ-35 (100)	11.1	55.9	12.4	4.7	11.9	14.3	0.9	1.32
H-SSZ-35 (500)	3.3	65.8	0.0	0.0	11.2	14.3	8.8	0.37
Cr/H-SSZ-35 (500)	33.8	40.0	1.4	7.3	16.1	24.2	11.0	5.44
H-SSZ-35 (1000)	1.5	46.1	0.0	5.6	15.6	22.1	10.5	0.23
Cr/H-SSZ-35 (1000)	16.7	24.6	0.0	10.1	16.4	32.6	16.4	2.74
H-ZSM-12 (200)	18.8	76.9	4.3	2.9	7.5	8.5	0.0	1.41
Cr/H-ZSM-12 (200)	12.7	45.9	2.5	8.0	20.6	22.4	0.6	2.62
H-Beta (27)	48.1	91.2	3.8	0.7	2.0	2.5	0.0	0.96
Cr/H-Beta (27)	7.7	77.6	2.3	3.9	7.6	8.7	0.0	0.59
H-ZSM-5 (29)	83.4	90.7	5.3	0.5	1.6	1.8	0.1	1.33
Cr/H-ZSM-5 (29)	86.9	93.4	4.7	0.3	0.8	0.8	0.0	0.70
H-mordenite (18.3)	85.8	96.0	2.4	0.0	0.7	0.9	0.0	0.60
Cr/H-mordenite (18.3)	61.5	83.9	10.8	0.2	2.1	2.9	0.0	1.29
Cr/USY (360)	6.2	20.2	0.0	12.7	19.0	37.9	10.3	1.18
SiO_2	0.9	99.9	0.0	0.0	0.0	0.0	0.0	0.0
Cr/SiO_2	16.5	18.6	0.0	10.8	0.0	45.3	25.3	0.0

Number in parenthesis stands for Si/Al_2 ratio.

found to be active in this reaction. The butane conversion was in the order: H-mordenite ($Si/Al_2 = 18.3$) > H-ZSM-5 ($Si/Al_2 = 29$) > H-SSZ-35 ($Si/Al_2 = 40$) > H-Beta ($Si/Al_2 = 27$) > H-ZSM-12 ($Si/Al_2 = 200$) > H-SSZ-35 ($Si/Al_2 = 100$) > H-SSZ-35 ($Si/Al_2 = 500$) > H-SSZ-35 ($Si/Al_2 = 1000$). However, these zeolite supports showed C_1–C_3 hydrocarbon formations to predominate over C_4 products, and the selectivity of C_4 compounds such as isobutene was low. The loading of Cr onto zeolite supports improved the selectivity of C_4 compounds. In particular, Cr catalysts supported on H-SSZ-35 ($Si/Al_2 = 100, 500, 1000$) showed increased conversion as well as the selectivity of isobutene. In the case of H-SSZ-35 ($Si/Al_2 = 500, 1000$), the loading of Cr improved the yields of isobutene (conversion of butane × selectivity of isobutene). However, other catalyst systems showed improved isobutene selectivity and decreased butane conversion. On the other hand, in the case of the Cr/H-ZSM-5 ($Si/Al_2 = 29$) catalyst, the conversion of butane increased somewhat, while the selectivity of isobutene decreased.

Thus, zeolite catalysts were found to have catalytic activity for the isomerization and dehydrogenation of butane into other C_4 compounds, such as isobutene. In most cases of zeolite supports, the selectivity of C_4 compounds, especially isobutene, was improved by the addition of Cr. In the case of H-SSZ-35, an increased Si/Al_2 ratio resulted in a decreased conversion of butane and increased selectivity of dehydrogenated compounds, such as isobutene. These indicated that there could be a correlation between the solid acidity of the support and the ability for dehydrogenation. The effect of Cr-loading on the conversion of butane was dependent on the supports used; however, the selectivity of dehydrogenated products was improved by the addition of Cr.

On the other hand, SiO_2 was almost inactive, while Cr/SiO_2 showed a high conversion of butane and a high selectivity of dehydrogenated C_4 products. However, no isomerized products (isobutane and isobutene) were detected. These results suggest that Cr_2O_3 promotes the dehydrogenation of butane, but does not promote its isomerization;[1–3] it also seems likely that skeletal isomerization takes place over the zeolite supports, and that dehydrogenation occurs over both Cr_2O_3 particles and zeolite supports.

Figure 4 shows the conversion of butane and the selectivity of isobutene over Cr catalysts supported on zeolites at 500 °C. Here, the number next to each symbol stands for the Si/Al_2 ratio of the zeolite support. Cr/H-SSZ-35 ($Si/Al_2 = 500$) showed a moderate conversion of butane (33.8%) and selectivity of isobutene (16.1%); as a result, the yield of isobutene (conversion of butane × selectivity of isobutene) was 5.44%, the highest among the Cr-supported catalysts used in this study. It is characteristic of H-SSZ-35 type zeolites that Cr catalysts supported on zeolites with low Si/Al_2 ratios (40, 100) show a lower conversion of butane than most other kinds of zeolites, possibly attributable to the weaker solid acidity of H-SSZ-35 than other zeolite supports, which leads to a low rate of cracking of butane. Moreover, the micropore structure of the zeolite supports affects the selectivity of isobutene, suggesting that H-SSZ-35 has a high shape-selectivity for the formation of isobutene.

As shown in Table 2, the selectivity of dehydrogenated C_4 products (1-butene, isobutene, 2-butenes, and 1,3-butadiene) over Cr/H-SSZ-35 ($Si/Al_2 = 500$) at 500 °C was 58.6%, and the yield was 19.8%, the highest of the catalysts employed. On the other hand, the selectivity of isomerized C_4 products (isobutane and isobutene) over Cr/H-SSZ-35 ($Si/Al_2 = 500$) was only 17.5%. These findings indicate that Cr/H-SSZ-35 ($Si/Al_2 = 500$) has high activity for dehydrogenation and moderate activity for the isomerization of butane.

Figure 5 shows the conversion of butane and the selectivity of each C_4 product over Cr/H-SSZ-35 ($Si/Al_2 = 500$) at each

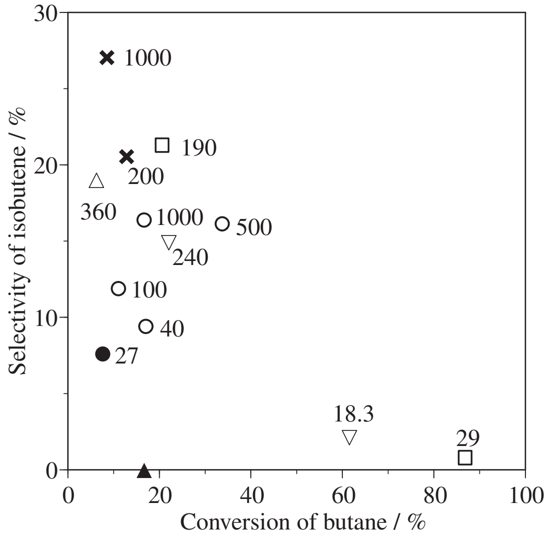

Fig. 4. Conversion of butane and selectivity of isobutene over Cr-supported catalysts (Cr = 10 wt %) at 500 °C. (○) Cr/H-SSZ-35, (△) Cr/USY, (□) Cr/H-ZSM-5, (▽) Cr/H-mordenite, (●) Cr/H-Beta, (×) Cr/H-ZSM-12, (▲) Cr/SiO$_2$. Number next to symbol stands for Si/Al$_2$ ratio.

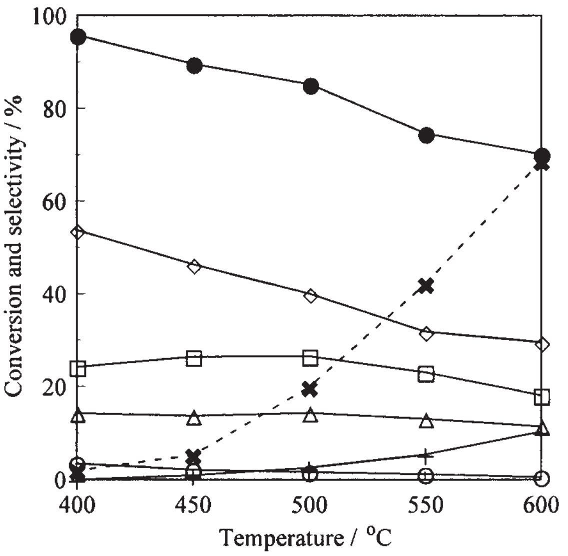

Fig. 5. Catalytic performance of the Cr/H-SSZ-35 (Si/Al$_2$ = 500, Cr = 10 wt %) catalyst as a function of temperature. Conversion: (×) butane. Selectivity: (●) C$_4$ products, (○) isobutane, (△) 1-butene, (□) isobutene, (◇) 2-butenes, (+) 1,3-butadiene.

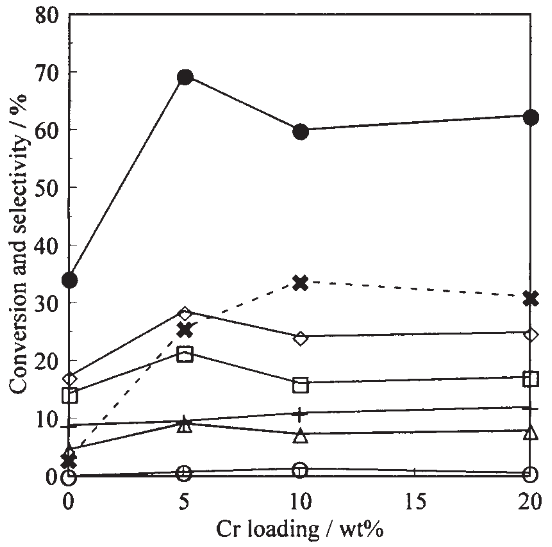

Fig. 6. Catalytic performance of the Cr/H-SSZ-35 (Si/Al$_2$ = 500) catalyst as a function of Cr-loading at 500 °C. Conversion: (×) butane. Selectivity: (●) C$_4$ products, (○) isobutane, (△) 1-butene, (□) isobutene, (◇) 2-butenes, (+) 1,3-butadiene.

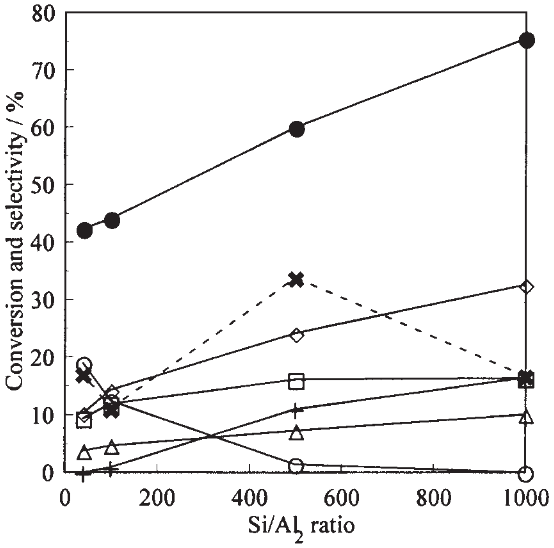

Fig. 7. Catalytic performance of the Cr/H-SSZ-35 (Cr = 10 wt %) catalyst as a function of Si/Al$_2$ ratio at 500 °C. Conversion: (×) butane. Selectivity: (●) C$_4$ products, (○) isobutane, (△) 1-butene, (□) isobutene, (◇) 2-butenes, (+) 1,3-butadiene.

temperature between 400 °C and 600 °C. The conversion of butane increased with increasing temperature (×), while the selectivity of C$_4$ products decreased (●). These results suggest that high temperature favors the cracking of butane over its dehydrogenation and isomerization. With increasing temperature, the selectivity of 2-butenes gradually decreased, while the selectivity of 1,3-butadiene increased. The selectivity of 1-butene remained unchanged with temperature, but the selectivity of isobutene increased with temperatures below 500 °C and decreased above 500 °C. These findings suggest that at high temperature, dehydrogenation predominates over skeletal isomerization.

The effect of Cr-loading is shown in Fig. 6. Below 10 wt % of Cr-loading, the conversion of butane increased with increased Cr-loading, and leveled off beyond 10 wt % (×). On the other hand, the selectivity of C$_4$ products, especially isobutene, leveled off above 5 wt % of Cr-loading (●). These results suggest that the conversion of butane was affected by Cr-loading, and that excessive loading of Cr did not always lead to a high conversion of butane.

The effect of the Si/Al$_2$ ratio is shown in Fig. 7. As a result

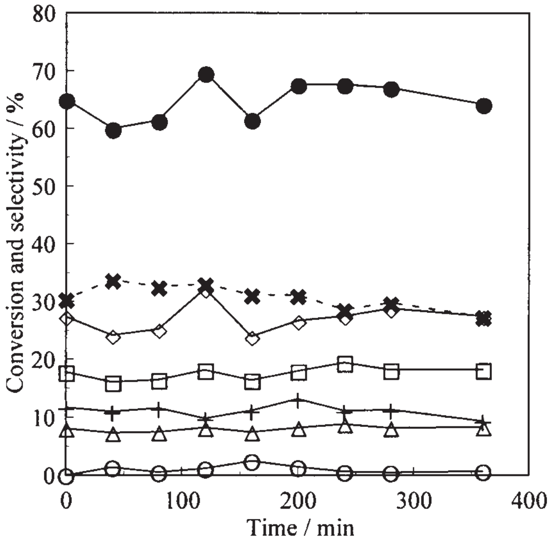

Fig. 8. Catalytic performance of the Cr/H-SSZ-35 (Si/Al_2 = 500, Cr = 10 wt %) catalyst as a function of time at 500 °C. Conversion: (×) butane. Selectivity: (●) C_4 products, (○) isobutane, (△) 1-butene, (□) isobutene, (◇) 2-butenes, (+) 1,3-butadiene.

of increasing the Si/Al_2 ratio, the selectivity of the total C_4 products and dehydrogenated products (1-butene, isobutene, 2-butenes, and 1,3-butadiene) increased, while the selectivity of isobutane decreased. On the other hand, the correlation between the Si/Al_2 ratio and the conversion of butane was not clear. It seems that solid acidity is needed for the isomerization of butane, while an excess amount of solid acid leads to the cracking of butane, rather than isomerization.

Wang et al. reported on the dehydrogenation and isomerization of butane on Cr-supported WO_3–ZrO_2, but the catalytic activity decreased with the reaction time as a result of carbon deposition.[7,8] As shown in Fig. 8, the C_4 product selectivity over Cr/H-SSZ-35 catalyst (Si/Al_2 = 500) remained unchanged at 500 °C for 6 h (●), although butane conversion showed a slight decrease (×).

The diameter of 10MR of H-SSZ-35 was 5.5 × 6.1 Å, and that of 18MR was 12.5 × 9 Å, much larger than the size of the isobutene molecule. The other zeolites used (H-mordenite, H-ZSM-5, H-Beta) also have micropores larger than the size of isobutene molecules; however, they do not show a yield of isobutene higher than that from H-SSZ-35. This suggests that the characteristic microstructure of H-SSZ-35 provides shape-selectivity for butane conversion to isobutene. Moreover, H-SSZ-35 type zeolites have a large micropore volume and weaker solid acidity than other kinds of zeolites in TPD. We believe that these characteristics of H-SSZ-35 led to the highest isobutene yield for butane conversion.

The reaction path was postulated as follows: butane was dehydrogenated over a zeolite support or Cr_2O_3 particles, and a part of the dehydrogenated products were skeletally isomerized to isobutene over the zeolite support. The strong acidity of the zeolite support favors the cracking of butane, and the loading of Cr on zeolite improves the dehydrogenation, with the result that the cracking of butane was suppressed.

These findings on the catalytic activity and lifetime provide clear evidence that H-SSZ-35 type zeolite possesses the possibility of use as a support for the production of isobutene by the dehydrogenation and isomerization of butane.

Conclusions

Zeolites can catalyze the dehydrogenation and isomerization of butane to isobutene. However, zeolite supports, especially those having a low Si/Al_2 ratio, favor the cracking of butane over dehydrogenation and isomerization, due to their strong solid acidity. The loading of Cr on zeolite supports enhances the dehydrogenation and isomerization of butane. Of the Cr catalysts supported on zeolites, Cr/H-SSZ-35 (Si/Al_2 = 500) showed moderate butane conversion and isobutene selectivity and maintained its catalytic activity at 500 °C for 6 h. As a result, the yield of isobutene (5.44%) was the highest among the catalysts used in this study.

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