Dehydrogenation and isomerization of *n*-butane or isobutane over Cr catalysts supported on zeolites

Megumu Inaba [a,*], Kazuhisa Murata [a], Masahiro Saito [a], Isao Takahara [a], Naoki Mimura [a],
Hideaki Hamada [a], and Yohei Kurata [b]

[a] *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*
[b] *Central Research Laboratory, Showa Denko K.K., 13-9, Siba Daimon 1-Chome, Minato-ku, Tokyo 105-8518, Japan*

Received 5 July 2002; accepted 14 September 2002

Dehydrogenation and isomerization of *n*-butane or isobutane into isobutene over Cr catalysts supported on zeolites were investigated. We found that Cr catalyst supported on H-SSZ-35-type zeolite, having one-dimensional cage-type channel structure, was very effective for this reaction and the yield of isobutene was 5.44% from *n*-butane and 9.57% from isobutane. In this reaction, it is suggested that dehydrogenation of butanes is accelerated by Cr_2O_3 loading, and solid acidity of the zeolite support favors isomerization.

KEY WORDS: H-SSZ-35-type zeolites; *n*-butane; dehydrogenation and isomerization; isobutene; Cr catalyst.

1. Introduction

Isobutene is an important intermediate for many common petrochemicals and plastics and, in order to synthesize isobutene, dehydrogenation of isobutane [1–3] and isomerization of butenes [4–6] had been studied quite extensively. For dehydrogenation of isobutane, it has been reported that Cr oxide-based catalysts are effective. Hoang *et al.* [1] have investigated 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 $Pr_2(CO_3)_3$). Rossi *et al.* [2] used CrO_x/ZrO_2, $CrO_x/\gamma\text{-}Al_2O_3$, and CrO_x/SiO_2, and Grzybowska *et al.* [3] also used $CrO_x/\gamma\text{-}Al_2O_3$.

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

However, through these methods, two processes (dehydrogenation and isomerization) are still required to obtain isobutene from *n*-butane, and, from the standpoint of energy saving, simultaneous dehydrogenation and isomerization of *n*-butane to isobutene is highly desirable. Wang *et al.* have reported the simultaneous dehydrogenation and isomerization of *n*-butane to isobutene over Cr-based ZrO_2 catalysts in oxidative conditions [7] and Cr-based WO_3-promoted catalysts in non-oxidative conditions [8]. In these reports, it has been found that $Cr/WO_3\text{-}ZrO_2$ had the highest activity for dehydrogenation and isomerization of *n*-butane to isobutene under both oxidative and non-oxidative conditions. Kishida and coworkers [9] have investigated the direct conversion of butane to isobutene over metal oxide catalysts supported on γ-alumina and found that, of the 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.

On the other hand, zeolites have micropores with ordered size and solid acidity, and there has been growing interest in the application of zeolites as catalysts as well as molecular sieves. Therefore, dehydrogenation and isomerization of *n*-butane to isobutene over zeolite catalysts have been also studied extensively. Kishida and coworkers [10] also found that Pt catalysts supported on zeolite-like materials were more effective for the direct conversion of butane to isobutene than Ga(III) catalysts supported on corresponding materials, and Pt catalysts supported on MFI-type ferrisilicate produced isobutene in the highest yield. On the other hand, Byggningsbacka *et al.* [11] have reported the combination of Zn-modified K-ZSM-5 with a ZSM-22 system for the simultaneous dehydrogenation and isomerization of *n*-butane to isobutene. In their report, *n*-butene was obtained over Zn-modified K-ZSM-5 dehydrogenation catalyst, and isobutene was obtained from *n*-butene over ZSM-22 skeletal isomerization catalyst.

---

[*] To whom correspondence should be addressed.
E-mail: mg.inaba@aist.go.jp

1011-372X/02/1200-0273/0 © 2002 Plenum Publishing Corporation

In our study, Cr catalysts supported on zeolites were prepared, and their effects on the conversion of *n*-butane and selectivity of products were investigated.

2. Experimental

As zeolite supports, H-SSZ-35, H-Beta, H-ZSM-5 and H-mordenite were used. Wagner *et al.* [12,13] hydrothermally synthesized H-SSZ-35-type zeolites by using cyclic and polycyclic quaternized amine molecules as structure-directing agents (SDAs). In this study, however, H-SSZ-35 with high crystallinity was hydrothermally synthesized with *cis,cis,cis*-N-methyl-hexahydrojulolidinium hydroxide as the SDA in a short time. Other zeolite supports such as H-Beta, H-ZSM-5, and H-mordenite were obtained commercially (Toso). Before use, these zeolites were also calcined at 500 °C for 6 h in air.

Cr catalysts supported on zeolites were prepared by the impregnation method. Typically, the loading of Cr was 10 wt%, and varied from 5 to 20 wt%. Chromium(III) nitrate nonahydrate (Wako Pure Chemical) was used as the source of Cr. 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 comparison, Cr catalyst supported on silica was prepared by same method.

As characterization of Cr catalysts supported on zeolites, powder X-ray diffraction analysis of Cr-supported catalysts reduced in the flow of hydrogen at 600 °C was performed with Mac Science, M18XHF^{22}-SRA (Cu K_α radiation), and the diameter of Cr particles was calculated from the results of XRD patterns.

Catalytic activity was measured with a fixed-bed reactor. The catalyst weighed 1 g. Before 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) equipped with Molecular Sieve 5A and a Porapak Q column. Two detectors were used: TCD was used to detect gaseous products such as hydrogen, and FID to detect hydrocarbons. The reactant gas contained $n\text{-}C_4H_{10}$ (20%) and Ar (80%) and the gas flow rate was 60 cm^3 min^{-1}. To investigate the catalytic activity and reaction pathway, the reaction of $iso\text{-}C_4H_{10}$ instead of $n\text{-}C_4H_{10}$ was also carried out. The reaction temperature was changed from 400 to 600 °C at every 50 °C.

3. Results and discussion

Table 1 shows conversion of *n*-butane and selectivity of each product over zeolite supports alone and Cr catalysts supported on zeolites (Cr = 10 wt%) at 500 °C . For comparison, the conversion and the selectivity over silica support and Cr catalyst supported on silica are also shown in same table. In almost all cases, zeolite supports alone were found to be active for this reaction. However, these zeolite supports showed predominant formations of C_1–C_3 hydrocarbons over C_4 products and selectivity of C_4 compounds such as isobutene was low. In the case of H-SSZ-35 support, the increasing Si/Al$_2$ ratio led to the decreased conversion of *n*-butane but led to increased selectivity of dehydrogenated C_4 products, especially isobutene, while the selectivity of isobutane decreased (Nos. 1, 3, and 5). It seems that solid acidity is needed for isomerization of *n*-butane, while an excess amount of solid acid leads to decomposition of *n*-butane rather than isomerization.

The effect of loading of Cr on conversion of *n*-butane depended on the kind of zeolite supports. Cr catalysts supported on H-SSZ-35 (Si/Al$_2$ = 40), H-Beta (Si/Al$_2$ = 27)

Table 1
Catalytic performance of the various zeolite catalysts in conversion of *n*-butane at 500 °C.

No.	Conv. (%)	Selectivity (%)								
		C_1	C_2	C_3	$iso\text{-}C_4H_{10}$	$1\text{-}C_4H_8$	$iso\text{-}C_4H_8$	$trans\text{-}2\text{-}C_4H_8$	$cis\text{-}2\text{-}C_4H_8$	$1,3\text{-}C_4H_6$
(1)	50.4	5.5	24.0	57.6	8.0	0.7	2.0	1.3	0.9	0.0
(2)	17.1	4.1	14.2	39.4	18.9	3.8	9.4	6.1	4.2	0.0
(3)	8.6	11.4	31.9	28.7	4.6	0.0	6.6	5.9	4.0	6.9
(4)	11.1	7.0	14.4	34.5	12.4	4.7	11.9	8.0	6.3	0.9
(5)	3.3	13.9	36.4	15.5	0.0	0.0	11.2	8.6	5.7	8.8
(6)	33.8	15.1	10.5	14.4	1.4	7.3	16.1	13.6	10.6	11.0
(7)	48.1	10.6	38.2	42.4	3.8	0.7	2.0	1.4	1.1	0.0
(8)	7.7	10.4	21.6	45.6	2.3	3.9	7.6	5.2	3.5	0.0
(9)	83.4	10.7	27.9	52.1	5.3	0.5	1.6	1.0	0.8	0.1
(10)	86.9	10.5	26.2	56.7	4.7	0.3	0.8	0.5	0.3	0.0
(11)	85.8	15.2	39.1	41.7	2.4	0.0	0.7	0.6	0.3	0.0
(12)	61.5	5.7	16.9	61.3	10.8	0.2	2.1	1.5	1.4	0.0
(13)	0.9	31.6	18.4	49.9	0.0	0.0	0.0	0.0	0.0	0.0
(14)	16.5	11.4	3.8	3.4	0.0	10.8	0.0	24.1	21.2	25.3

(1) H-SSZ-35 (Si/Al$_2$ = 40), (2) Cr/H-SSZ-35 (Si/Al$_2$ = 40), (3) H-SSZ-35 (Si/Al$_2$ = 100), (4) Cr/H-SSZ-35 (Si/Al$_2$ = 100), (5) H-SSZ-35 (Si/Al$_2$ = 500), (6) Cr/H-SSZ-35 (Si/Al$_2$ = 500), (7) H-Beta (Si/Al$_2$ = 27), (8) Cr/H-Beta (Si/Al$_2$ = 27), (9) H-ZSM-5 (Si/Al$_2$ = 29), (10) Cr/H-ZSM-5 (Si/Al_2 = 29), (11) H-mordenite (Si/Al$_2$ = 18.3), (12) Cr/H-mordenite (Si/Al$_2$ = 18.3), (13) SiO_2, (14) Cr/SiO_2.

and H-mordenite ($Si/Al_2 = 18.3$) showed decreased conversion of *n*-butane (Nos. 2, 8, and 12). On the other hand, Cr catalysts on H-SSZ-35 ($Si/Al_2 = 100$, 500), H-ZSM-5 ($Si/Al_2 = 29$), and SiO_2 showed improved conversion of *n*-butane (Nos. 4, 6, 10, and 14). This result suggested that zeolites with higher Si/Al_2 ratio (including SiO_2) improved the conversion of *n*-butane by loading of Cr and, on the other hand, zeolites with lower Si/Al_2 ratio decreased the conversion by loading of Cr. In almost all cases, loading of Cr on zeolite supports improved the selectivity of C_4 compounds, especially isobutene, except for the case of H-ZSM-5 ($Si/Al_2 = 29$) (No. 10). Moreover, in the case of Cr catalyst supported on H-SSZ-35, the result was similar to the case of H-SSZ-35 supports alone. Increasing the Si/Al_2 ratio, the selectivity of total C_4 products and dehydrogenated products (1-butene, isobutene, *trans*-2-butene, *cis*-2-butene and 1,3-butadiene) increased, while the selectivity of isobutane decreased. However, the correlation between Si/Al_2 ratio and conversion of *n*-butane was not clear (Nos. 2, 4, and 6). On the other hand, SiO_2 was almost inactive, while Cr catalyst supported on SiO_2 showed high conversion of *n*-butane and high selectivity of dehydrogenated C_4 products. However, isomerized products (isobutane and isobutene) were not detected at all (No. 14).

Thus, Cr/zeolite catalysts were found to be effective for simultaneous isomerization and dehydrogenation of *n*-butane into other C_4 compounds such as isobutene. In almost all cases of zeolite supports, the increased Si/Al_2 ratio resulted in not only a decrease in the decomposition activity of *n*-butane, but an increase in the dehydrogenation and, as a result, the conversion of *n*-butane was decreased and selectivity of the dehydrogenated compounds such as isobutene was increased. Thus, there could be a correlation between solid acidity of the support and capability of dehydrogenation and/or decomposition.

The selectivity of dehydrogenated products was improved by the addition of Cr. The results of Cr/SiO_2 suggested that Cr promotes dehydrogenation of *n*-butane, while it does not promote isomerization of *n*-butane [1–3], and the isomerization could take place over the zeolite supports, and dehydrogenation and isomerization occur over Cr species/zeolite systems.

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, and the size of Cr_2O_3 particles calculated from the XRD pattern was about 30 nm, larger than the diameter of micropores of zeolite. These results indicated that Cr_2O_3 particles could not be involved inside the micropores of zeolite. There is a possibility that Cr^{6+} species exist inside the micropores. However, even if Cr^{6+} species exist, it seems that the amount of Cr^{6+} species is negligible and they do not influence catalytic activity, since below 5 wt% of Cr loading, the existence of Cr affected the catalytic activity of Cr-supported catalysts (see figure 4). Cr^{6+} species may be fully saturated even at low Cr loading, and they do not increase by increasing Cr loading. From this, it seems that Cr^{6+} species do not act as a catalytic active site, but Cr_2O_3 particles do.

Cr/H-SSZ-35 ($Si/Al_2 = 500$) showed moderate conversion of *n*-butane (33.8%) and selectivity of isobutene (16.1%) and, as a result, the yield of isobutene (conversion of *n*-butane × selectivity of isobutene) was 5.44%, the highest among the Cr-supported catalysts used in this study (No. 6). Also, the selectivity of dehydrogenated C_4 products was 58.6% and the yield was 19.8%, also the highest of the catalysts employed. However, the selectivity of isomerized C_4 products (isobutane and isobutene) was only 17.5%. These findings indicate that Cr/H-SSZ-35 ($Si/Al_2 = 500$) has moderate activity for both the dehydrogenation and isomerization of *n*-butane.

The conversion of *n*-butane and the selectivity of each C_4 product over Cr/H-SSZ-35 ($Si/Al_2 = 500$, $Cr = 10$ wt%) at each temperature between 400 and 600 °C are shown in figure 1. Conversion of *n*-butane increased

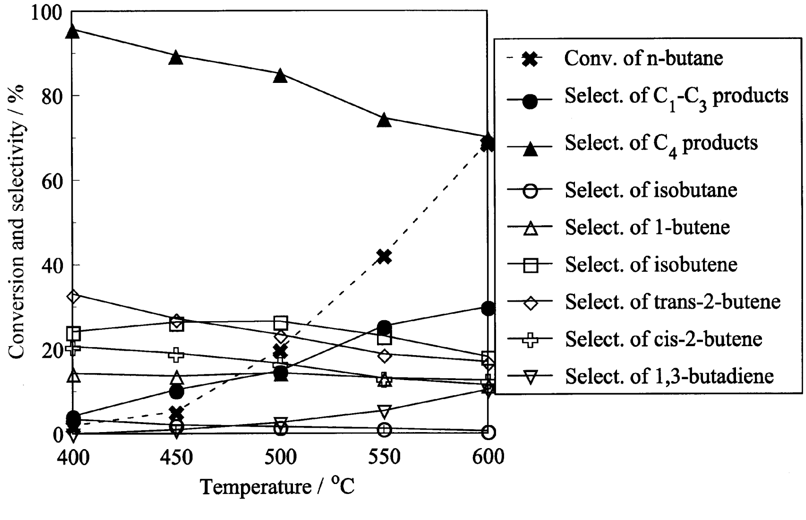


Figure 1. Effect of reaction temperature on conversion of *n*-butane and selectivity of each product over Cr/H-SSZ-35 ($Si/Al_2 = 500$, $Cr = 10$ wt%) catalyst.

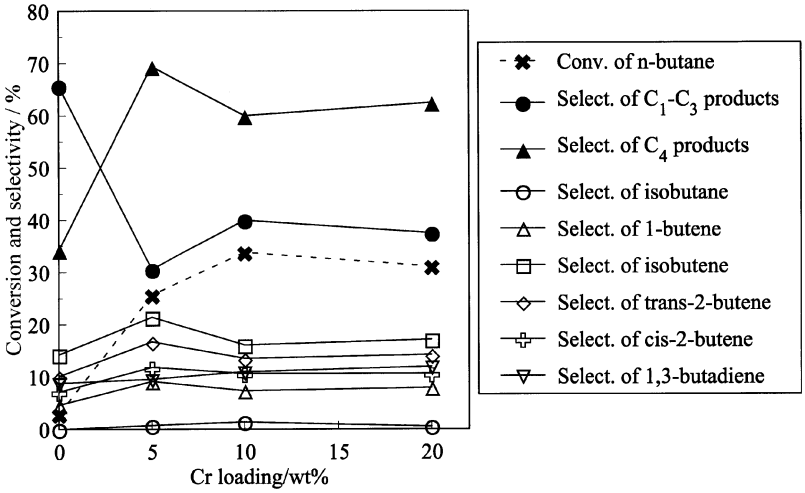


Figure 2. Effect of Cr loading on conversion of *n*-butane and selectivity of each product over Cr/H-SSZ-35 ($Si/Al_2 = 500$) catalyst at 500 °C.

with increasing temperature (✖), while selectivity of C_4 products decreased (▲). These results suggested that high temperature favors decomposition of *n*-butane over dehydrogenation and isomerization of *n*-butane. With increasing temperature, selectivity of *trans*-2-butene and *cis*-2-butene gradually decreased, while the selectivity of 1,3-butadiene increased. The selectivity of 1-butene remained unchanged with temperature, and the selectivity of isobutene slightly increased with temperature below 500 °C, and decreased above 500 °C. These findings suggested that, at high temperature, dehydrogenation predominates over isomerization.

The effect of Cr loading on conversion of *n*-butane and selectivity of each product is shown in figure 2. Here, Cr/H-SSZ-35 ($Si/Al_2 = 500$) was used and the reaction temperature was 500 °C. Below 10 wt% of Cr loading, conversion of *n*-butane increased with the increase in the Cr loading and it leveled off above 10 wt% (✖). On the other hand, selectivity of C_4 products, especially isobutene, leveled off above 5 wt% of Cr loading (▲). These results suggested that conversion of *n*-butane was affected by Cr loading and excess loading of Cr did not always lead to high conversion of *n*-butane.

The conversion of isobutane was also carried out. Table 2 shows the conversion of isobutane and selectivity of each product over several kinds of zeolites and Cr catalysts supported on zeolites (Cr = 10 wt%) at 500 °C. In almost all cases, conversion of isobutane was higher than that of *n*-butane using the same zeolite support, suggesting that isobutane is more reactive than *n*-butane and dehydrogenation and decomposition predominantly occurred over isomerization. In fact, as in the case of H-SSZ-35 support, increasing the Si/Al_2 ratio led to decreased conversion of isobutane, but to improved selectivity of dehydrogenated C_4 products, especially isobutene, while selectivity of *n*-butane decreased (Nos. 1 and 3). Loading of Cr on zeolite supports improved the selectivity of dehydrogenated C_4 products; especially the selectivity of isobutene improved

Table 2

Catalytic performance of the various zeolite catalysts in conversion of isobutane at 500 °C.

No.	Conv. (%)	Selectivity (%)								
		C_1	C_2	C_3	*n*-C_4H_8	1-C_4H_8	*iso*-C_4H_8	*trans*-2-C_4H_8	*cis*-2-C_4H_8	1,3-C_4H_6
(1)	61.0	4.7	17.5	51.6	18.2	1.1	3.4	1.9	1.4	0.0
(2)	59.4	5.2	14.4	48.8	17.0	1.9	6.6	3.5	2.6	0.1
(3)	4.5	18.0	5.9	21.7	0.0	4.7	17.6	13.7	8.2	10.4
(4)	30.2	6.6	6.9	17.1	1.6	7.1	31.7	13.9	10.4	4.7
(5)	76.0	12.0	28.8	45.2	4.6	1.3	3.9	2.5	1.7	0.0
(6)	36.7	7.4	15.3	42.9	9.0	3.6	10.8	6.4	4.6	0.0
(7)	96.7	28.3	30.7	37.9	1.1	0.2	0.8	0.6	0.4	0.0
(8)	51.9	15.4	30.8	39.2	2.7	1.8	4.9	3.0	2.0	0.2
(9)	66.8	33.2	42.1	8.4	13.4	0.4	1.2	0.8	0.6	0.0
(10)	70.7	9.8	20.2	48.0	15.6	0.8	2.7	1.7	1.3	0.1

(1) H-SSZ-35 ($Si/Al_2 = 40$), (2) Cr/H-SSZ-35 ($Si/Al_2 = 40$), (3) H-SSZ-35 ($Si/Al_2 = 500$), (4) Cr/H-SSZ-35 ($Si/Al_2 = 500$), (5) H-Beta ($Si/Al_2 = 27$), (6) Cr/H-Beta ($Si/Al_2 = 27$), (7) H-ZSM-5 ($Si/Al_2 = 29$), (8) Cr/H-ZSM-5 ($Si/Al_2 = 29$), (9) H-mordenite ($Si/Al_2 = 18.3$), (10) Cr/H-mordenite ($Si/Al_2 = 18.3$).

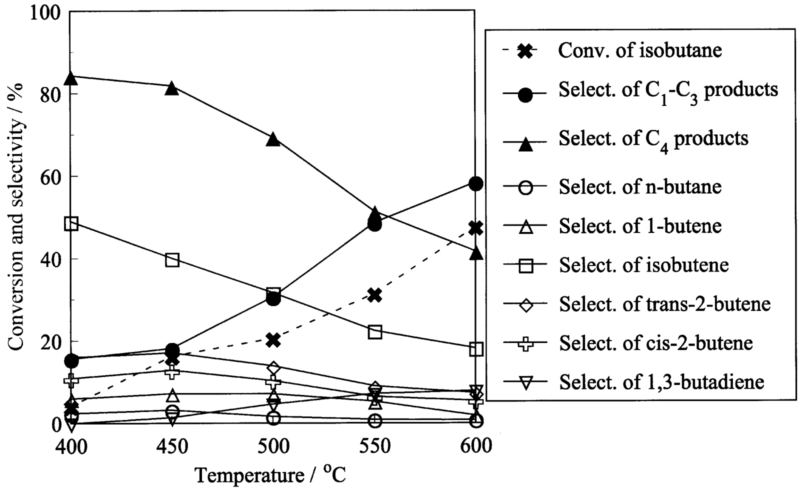


Figure 3. Effect of reaction temperature on conversion of isobutane and selectivity of each product over Cr/H-SSZ-35 ($Si/Al_2 = 500$, Cr = 10 wt%) catalyst.

in all runs of table 2, suggesting that dehydrogenation rather than isomerization improved by Cr loading. In the case of Cr catalysts supported on H-SSZ-35, similar results to H-SSZ-35 supports alone were obtained. Increasing the Si/Al_2 ratio, the selectivity of total C_4 products and dehydrogenated products (1-butene, isobutene, *trans*-2-butene, *cis*-2-butene, and 1,3-butadiene) increased, especially that of isobutene, while the selectivity to *n*-butane and C_1–C_3 products decreased, whereas the conversion of isobutane decreased (Nos. 2 and 4). It seems that the excess amount of solid acid leads to decomposition of isobutane rather than dehydrogenation and isomerization. Thus, Cr catalysts supported on H-SSZ-35 ($Si/Al_2 = 500$) and H-mordenite ($Si/Al_2 = 18.3$) showed improved conversion of isobutane (Nos. 4 and 10), but other catalysts showed decreased conversion of isobutane (Nos. 2, 6, and 8).

Cr/H-SSZ-35 ($Si/Al_2 = 500$) revealed the highest selectivity of isobutene (31.7%) among the Cr-supported catalysts in table 2. Moreover, yield of isobutene (conversion of isobutane × selectivity of isobutene) was also the highest (9.57%), while conversion of isobutane was not especially high (30.2%). These results suggested that Cr/H-SSZ-35 ($Si/Al_2 = 500$) has a high activity for dehydrogenation of isobutane. In table 1, selectivity of isomerized products (isobutane and isobutene) from *n*-butane was 17.5% over Cr/H-SSZ-35 ($Si/Al_2 = 500$) at 500 °C, while in table 2, selectivity of isomerized products (*n*-butane, 1-butene, *trans*-2-butene, *cis*-2-butene, and 1,3-butadiene) from isobutane was 37.7% over the same catalyst.

The conversion of isobutane and the selectivity of each C_4 product over Cr/H-SSZ-35 ($Si/Al_2 = 500$) at each temperature between 400 and 600 °C are shown in figure 3. Conversion of isobutane increased with increasing temperature (✖), while selectivity of C_4 products decreased (▲). The decrease of selectivity of C_4 products was larger than that in the case of *n*-butane; for example,

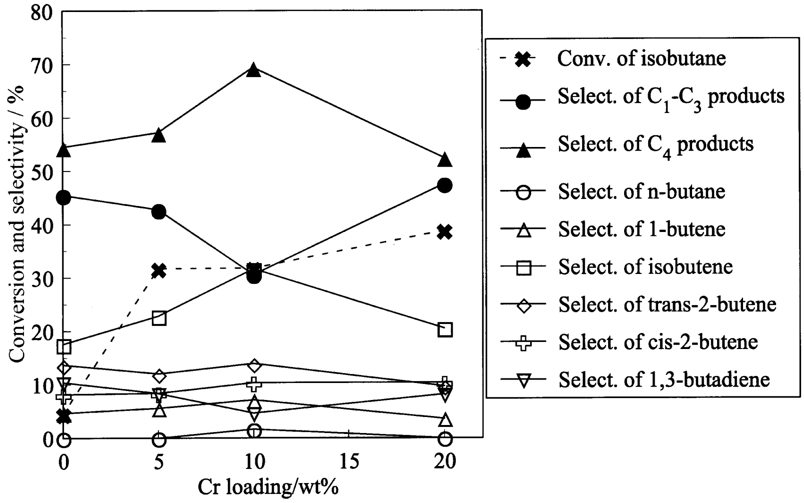
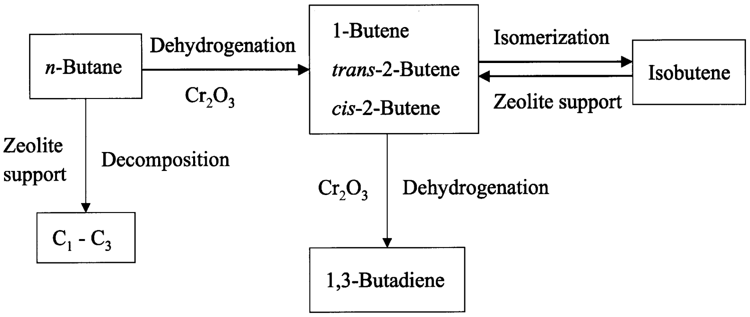


Figure 4. Effect of Cr loading on conversion of isobutane and selectivity of each product over Cr/H-SSZ-35 ($Si/Al_2 = 500$) catalyst at 500 °C.



Scheme 1. Supposed reaction pathway.

the selectivity was about 40% at 600 °C, while in the case of *n*-butane, the selectivity was about 70% at the same temperature. This result suggested that isobutane could be decomposed more easily than *n*-butane. Moreover, the Cr/H-SSZ-35 catalysts could be found to be active for not only isomerization from *n*-butenes to isobutene, but also for transformation from isobutene to *n*-butenes. Selectivity to isobutene was much higher than other C_4 products, suggesting that dehydrogenation of isobutane without isomerization could take place more easily than isomerization of isobutane with or without dehydrogenation. However, with increasing temperature, the selectivity of isobutene drastically decreased, suggesting that, even in the case of isobutane, higher temperature favors decomposition over dehydrogenation.

The effect of Cr loading on conversion of isobutane and selectivity of each product is shown in figure 4. Here, Cr/H-SSZ-35 ($Si/Al_2 = 500$) was used and the reaction temperature was 500 °C. Below wt% of Cr loading, conversion of isobutane increased with increase in the Cr loading and it leveled off above 5 wt% (✖). On the other hand, selectivity of isobutene, higher than that of other C_4 products, increased with increase in the Cr loading below 10 wt%, and decreased above 10 wt%. The selectivity to 1,3-butadiene decreased with increase in Cr loading until 10 wt% and thereafter increased again, suggesting that excessive loading of Cr leads to a deep dehydrogenation to 1,3-butadiene and, as a result, selectivity of isobutene decreased above 10 wt% of Cr loading.

The reaction path was postulated as follows (scheme 1): *n*-butane is dehydrogenated over zeolite support or Cr_2O_3 particles, and a part of the dehydrogenated products is isomerized to isobutene over zeolite support. Isomerization between *n*-butenes and isobutene is reversible. Strong acidity of the zeolite support favors the decomposition of *n*-butane, and loading of Cr on zeolite improves dehydrogenation and, as a result, the decomposition of *n*-butane is suppressed.

Wang *et al.* [7,8] reported the dehydrogenation and isomerization of *n*-butane on Cr-supported WO_3–ZrO_2, and the catalytic activity decreased with reaction time by deposition of carbon. As shown in figure 5, the selectivity of C_4 products over Cr/H-SSZ-35 catalyst ($Si/Al_2 = 500$) remained unchanged at 500 °C for 6 h (▲) although *n*-butane conversion was slightly decreased (✖). From these findings on the catalytic activity and lifetime, H-SSZ-35 was expected to be one of the promising

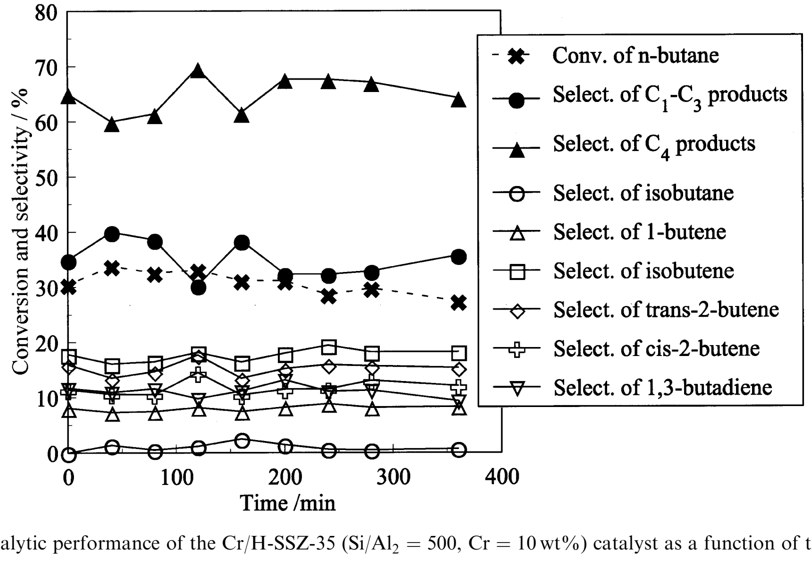


Figure 5. Catalytic performance of the Cr/H-SSZ-35 ($Si/Al_2 = 500$, Cr = 10 wt%) catalyst as a function of time at 500 °C.

supports for the production of isobutene by the dehydrogenation and the isomerization of *n*-butane.

4. Conclusions

For dehydrogenation and isomerization of *n*-butane to isobutene, zeolites were effective catalysts. However, a high acidity of zeolite support, especially having low Si/Al_2 ratio, favors decomposition of *n*-butane over dehydrogenation and isomerization. Loading of Cr on zeolite support enhanced dehydrogenation and isomerization of *n*-butane. Among the Cr catalysts supported on zeolites, Cr/H-SSZ-35 ($Si/Al_2 = 500$) had moderate *n*-butane conversion and isobutene selectivity and kept 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. H-SSZ-35-type zeolites have one-dimensional cage-type channel structure with pore openings that alternate between rings of 10 tetrahedral atoms (10MR) and 18 tetrahedral atoms (18MR), and large micropore volume. The diameter of 10MR of H-SSZ-35 is 5.5×6.1 Å, and that of 18MR is 12.5×9 Å, much larger than the size of the isobutene molecule. In the case of other zeolites (H-mordenite, H-ZSM-5, H-Beta), they have micropores larger than the size of the isobutene molecules. However, they did not show a yield of isobutene higher than H-SSZ-35. Therefore, it was suggested that the characteristic microstructure and large micropore volume of H-SSZ-35 gave the shape-selectivity for the *n*-butane conversion to isobutene.

Acknowledgment

This work was supported by the Ministry of Economy, Trade and Industry, for the project on Molecular Harmonized Materials.

References

[1] M. Hoang, J.F. Mathews and K.C. Pratt, Chemtech 9 (1999) 45.
[2] S.D. Rossi, M.P. Casaletto, G. Ferraris, A. Cimino and G. Minelli, Appl. Catal. A 167 (1998) 257.
[3] B. Crzybowska, J. Sloczynski, R. Grabowski, K. Wcislo, A. Kozlowska, J. Stoch and J. Zielinski, J. Catal. 178 (1998) 687.
[4] L.H. Gielgens, M.G.H. van Kampen, M.M. Broek, R. van Hardeveld and V. Ponec, J. Catal. 154 (1995) 201.
[5] J. Houzvicka, J.G. Nienhuis and V. Ponec, Appl. Catal. A 174 (1998) 207.
[6] G. Seo, S.H. Park and J.H. Kim, Catal. Today 44 (1998) 215.
[7] S. Wang, K. Murata, T. Hayakawa, S. Hamakawa and K. Suzuki, Energ. Fuel. 15 (2001) 384.
[8] S. Wang, K. Murata, T. Hayakawa, S. Hamakawa and K. Suzuki, Catal. Lett. 66 (2000) 13.
[9] Y. Takiyama, H. Nagata, M. Teshima, M. Kishida, H. Shimada and K. Wakabayashi, Sekiyu Gakkaishi 40 (1997) 199.
[10] Y. Takiyama, H. Nagata, M. Kishida and K. Wakabayashi, Sekiyu Gakkaishi 41 (1998) 80.
[11] R. Byggningsbacka, N. Kumar and L.-E. Lindfors, Catal. Lett. 55 (1998) 173.
[12] P. Wagner, S.I. Zones, M.E. Davis and R.C. Medrud, Angew. Chem. Int. Ed. 38 (1999) 1269.
[13] P. Wagner, Y. Nakagawa, G.S. Lee, M.E. Davis, S. Elomari, R.C. Medrud and S.I. Zones, J. Am. Chem. Soc. 122 (2000) 263.