

Introduction of a Small Amount of Chromium to Enhance the Catalytic Performance of SBA-15 for the Oxidative Dehydrogenation of Isobutane to Isobutene

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Abstract

Various solid oxide catalysts are active for the oxidative dehydrogenation of propane, but achieve yields of less than 2% when these were used for the oxidative dehydrogenation of isobutane to isobutene. An improved isobutene yield of 8% was obtained in the oxidative dehydrogenation of isobutane by using a folded-sheet mesoporous material (FSM-16) and mesoporous molecular sieve (MCM-41), with or without chromium via impregnation or template-ion exchange methods. Further activity enhancement, however, could not be attained. In the present study, chromium cations were introduced into the framework of SBA-15 using a direct synthesis method by mixing chromium nitrate with tetraethylorthosilicate in an aqueous solution with an initial pH of 1.5 and subsequent hydrothermal treatment. Loading the resultant catalyst, SBA-15, with a small amount of chromium (1.84 wt% Cr-SBA-15) increased the isobutene yield (15.4%) at 723 K, while a previous report showed that chromium oxide supported on SBA-15 (CrOx/SBA-15) prepared via incipient wetness impregnation had a lower isobutene yield (11%) at 813 K. To explain this improvement, the catalysts were characterized using X-ray diffraction, transmission electron microscopy, N₂ adsorption-desorption, and NH₃ temperature-programmed desorption. Cr-SBA-15 was found to have a large specific surface area (1,610 m²/g), although the structural and acidic nature of the catalyst was similar to the general properties of other mesoporous silicas. The conversion of Cr³⁺ species into Cr⁶⁺ on Cr-SBA-15 with the large specific surface area could affect the improvement of the oxidative dehydrogenation of isobutane to isobutene.

Introduction

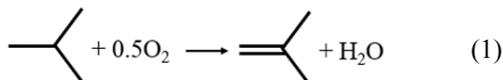
Among the production routes for methyl methacrylate (Ninomiya, 2014), which is an important chemical precursor for various advanced materials, such as acrylic plastics and methyl methacrylate-butadiene-styrene copolymers, we have focused on C₄ direct oxidation and C₄ oxidative esterification to overcome the serious problems associated with the classic acetone cyanohydrin (ACH) process. In the ACH process, acetone and cyanohydrin are the byproducts of phenol and acrylonitrile, respectively, which means that their production rates are dependent on those of the main products. Furthermore, the toxicity of cyanohydrin is a serious concern. In both C₄ direct oxidation and C₄ oxidative esterification, isobutene is produced, mainly via naphtha cracking, which is an energy-consuming process. More efficient methods for producing isobutene have been investigated using both the oxidative dehydrogenation (ODH) and dehydrogenation (DH) of isobutane, which is directly produced during petroleum refinement processes. The DH of isobutane has been investigated in various laboratories (Ohta *et al.*, 2004; Airaksinen *et al.*, 2005; Korhonen *et al.*,

2007), but, owing to its endothermic reaction, the DH process requires a higher reaction temperature than ODH. In our laboratory, oxygen was added into the feedstream to convert the endothermic reaction of DH into an exothermic reaction, as with ODH (Sattler *et al.*, 2014). Furthermore, the addition of oxygen can suppress the deposition of coke and subsequent rapid deactivation of the catalyst, which has been confirmed in the DH of isobutane.

In our laboratory, we have used various catalysts, such as magnesium vanadates and magnesium molybdates, for the ODH of isobutane (Eq. (1)). These are known as active catalysts for ODH, in this case, their use resulted in an isobutene yield of less than 2% at reaction temperatures below 723 K (Furukawa *et al.*, 2011). However, employing the template-ion exchange method (Yonemitsu *et al.*, 1997) to introduce chromium cations into various mesoporous silicas, such as FSM-16 (Sugiyama *et al.*, 2013, 2015; Ehiro *et al.*, 2015) and MCM-41 (Ehiro *et al.*, 2016a), significantly improved the isobutene yield to 8%. Relatively greater isobutene yields of 6–8% have been obtained by several methods: acid treatment of MCM-41, aluminum-doping of MCM-

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41 (Ehiro *et al.*, 2016b) prepared via the template-ion exchange method, and the use of calcium phosphates with or without impregnated chromium oxide (Ehiro *et al.*, 2017). Further enhancement of the yield beyond 8%, however, could not be accomplished. Therefore, the need for a more active catalyst is evident.



Selectivity for alkenes has been the general focus in the ODH of alkanes on solid catalysts. The yield of alkenes has been the focus of our previous studies, as shown above. Oxygen-lean conditions (oxygen-limited conditions), that is, an oxygen supply that is less than that estimated from stoichiometric equations, are generally employed in the ODH of alkanes, resulting in good selectivity for alkenes and low conversion of alkanes. Unfortunately, as the conversion is suppressed under such conditions, it is difficult to enhance the yield of alkenes, which is in contrast to our previous studies. Therefore, in the present study, we focused on the conversion and the selectivity under oxygen-rich conditions.

In the present study, SBA-15 was employed as a candidate catalyst for the ODH of isobutane. FSM-16, MCM-41, and SBA-15 are all examples of mesoporous silica based on a uniform hexagonal structure (Fukuoka *et al.*, 2006; Hoffmann *et al.*, 2006). However, the pore sizes of SBA-15 are greater than those of either FSM-16 or MCM-41 and can be controlled within a wider range (6–15 nm) by manipulating the interconnections between mesopores and micropores (Miyazawa and Inagaki, 2000; Zhao *et al.*, 2006). Wang *et al.* (2009) employed SBA-15 and chromium oxide supported on SBA-15 (CrOx/SBA-15) prepared via an incipient wetness impregnation as catalysts for the ODH of isobutane. The specific surface areas of the various forms of CrOx/SBA-15 are known to range from 556 to 787 m²/g, with a maximum isobutene yield of 11% at 813 K on 10wt% CrOx/SBA-15 (Wang *et al.*, 2009). This previous study focused on the reducible chromium species for the ODH of isobutane on CrOx/SBA-15, but the properties of chromium cations incorporated into the framework of SBA-15 were not investigated (Wang *et al.*, 2009).

In the present study, chromium was added to SBA-15 via a direct synthesis method (Cr-SBA-15) (Grieken *et al.*, 2009), in which chromium nitrate was mixed with tetraethylorthosilicate (TEOS) in an aqueous solution with an initial pH of 1.5 followed by hydrothermal synthesis. It is difficult to introduce heteroatoms into the mesoporous structure of SBA-15, but the direct synthesis method is known as an effective method to accomplish this (Grieken *et al.*, 2009). The present study showed that the template-ion exchange method could not be used with SBA-15, and, therefore,

the direct synthesis method was used to introduce chromium cations into the framework of SBA-15. In the present study, Cr-SBA-15 prepared via the direct synthesis method had a large specific surface area (1,610 m²/g), which resulted in an improved isobutene yield (15.4%) at 723 K.

1. Experimental

1.1 Catalyst preparation

SBA-15 was prepared via a procedure reported by Zhao *et al.* (1998) in consideration of the noteworthy level of reproducibility achieved using this method (Thielemann *et al.*, 2011). To 180 mL of 2 M HCl (Wako Pure Chemical Industries, Ltd.), 6 g of Pluronic 123 (P123) (Sigma-Aldrich Co. LLC.) and 6.72 g of KCl (Wako Pure Chemical Industries, Ltd.) were added. To this solution, 11.48 g of TEOS (Shin-Etsu Chemical Co., Ltd.) was added and stirred for 8 min, followed by aging at 317 K for 24 h under static conditions. Hydrothermal synthesis using the resultant solution was conducted in an autoclave at 373 K for 24 h without stirring. The solid product was recovered by filtration, washed, dried at 323 K for 2 days, and calcined at 823 K for 6 h (heating rate = 1 K/min) to yield SBA-15.

In preliminary experiments, various preparation methods, such as template-ion exchange (Yonemitsu *et al.*, 1997), incipient wetness impregnation (Wang *et al.*, 2009), and direct synthesis (Grieken *et al.*, 2009) were used to prepare chromium-added SBA-15. It should be noted that chromium could not be introduced into SBA-15 using template-ion exchange, although previous reports have noted that this method is suitable for introducing chromium into the frameworks of both FSM-16 and MCM-41 (Ehiro *et al.*, 2015, 2016a). The catalytic activity of Cr-SBA-15 prepared via incipient wetness impregnation (isobutene yield = 7.6%) was similar to those of FSM-16 and MCM-41 containing chromium. As Cr-SBA-15 prepared via direct synthesis resulted in significant activity, as shown below, we focused on Cr-SBA-15 in the present study. Details of the procedure for preparing Cr-SBA-15 via direct synthesis follow. To prepare Cr-SBA-15 at an atomic ratio of Si/Cr = 100, 8.60 g of TEOS and 0.165 g of Cr(NO₃)₃·9H₂O (Sigma-Aldrich Co. LLC.) were added to 10 mL of aqueous HCl at pH = 1.5. This mixture was stirred for 4 h at room temperature and then added to a second solution consisting of 4 g of P123 in 150 mL of aqueous HCl at pH = 1.5. The resultant mixture was stirred for 20 h at 313 K, followed by hydrothermal synthesis in an autoclave at 383 K for 24 h without stirring. The resultant solid product was recovered by filtration, washed, dried at 333 K for 1 day, and calcined at 823 K for 5 h (heating rate = 1.8 K/min) to yield Cr-SBA-15. Cr-SBA-15 prepared from precursor solutions with an atomic ratio of Si/Cr = x is hereafter referred to as Cr-SBA-15 (Si/Cr = x). Some catalysts were

analyzed via inductively coupled plasma atomic emission spectrometry (ICP-AES; SPS3520UV, SII Nanotechnology Inc.) to estimate the weight percent of chromium in the catalyst.

1.2 Catalyst characterization

X-ray diffraction (XRD; SmartLab/RA/INP/DX, Rigaku Co.), N₂ adsorption-desorption measurements (BELSORP-max12, MicrotracBEL), and transmission electron microscopy (TEM; JEM-2100F, JEOL Ltd.) were used to determine structural information about SBA-15 and Cr-SBA-15. Powder XRD patterns were obtained using monochromatized Cu K α radiation (40 kV, 40 mA). Before N₂ adsorption-desorption measurements at 77 K, the catalysts were pretreated at 473 K for 5 h under vacuum. The surface areas, S_{BET} and S_{micro}, corresponding to the BET specific surface area and micropore specific surface area, respectively, were calculated from the obtained isotherms using the BET equation and the t-plot method, respectively. The acidic properties of the catalysts were estimated using NH₃ temperature-programmed desorption (NH₃-TPD; BELCAT II, MicrotracBEL). For NH₃-TPD, the catalyst (50 mg) in a quartz tube was pretreated under 50 sccm of He at 773 K for 1 h and then cooled to 373 K. After maintaining this temperature for 10 min, the catalyst was treated with 50 sccm of 5% NH₃/He for 30 min. After these treatments, the catalyst was again maintained under a He flow (50.0 sccm) for 15 min. Subsequently, the catalyst was heated from 373 to 883 K at 10 K/min under 30 sccm of He. The desorption of NH₃ from the catalyst was recorded using a quadrupole mass spectrometer (BELMass, MicrotracBEL). The fragment peak at m/e = 16 was used to monitor the desorbed NH₃.

1.3 Catalytic activity testing

Catalytic activity tests were conducted in a fixed-bed continuous-flow reactor at atmospheric pressure. Each catalyst (0.25 g) was pelletized and sieved to 0.85–1.70 mm, and then fixed with quartz wool and pretreated with 12.5 mL/min of O₂ at 723 K for 1 h. After pretreatment, the catalytic activity test was started at 723 K by flowing 15 mL/min of a mixed gas of helium, isobutane, and oxygen into the reactor. The partial pressures were adjusted to $P(\text{He}) = 74.6$ kPa, $P(\text{i-C}_4\text{H}_{10}) = 14.4$ kPa, and $P(\text{O}_2) = 12.3$ kPa. These reaction conditions were used for all tests, unless otherwise stated. It should be noted that under these conditions, homogeneous oxidation was not observed at reaction temperatures below 763 K. However, homogeneous reactions were clearly detected at temperatures of 773 K, and higher, with ca. 50% of isobutane conversion at 823 K. The reaction was monitored using an online gas chromatograph (GC-8APT, Shimadzu Corp.) equipped with a TCD. For O₂, CH₄, and CO, a molecular sieve 5A (MS 5A, 0.2 m \times Φ

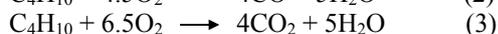
3 mm) was used in the column and for CO₂, C₂, C₃, and C₄ products, a Hayesep R column was used (2.0 m \times Φ 3 mm). The carbon balance between the reactant and the products was within $\pm 5\%$. The selectivity for each product and the conversion of isobutane were calculated on a carbon basis.

2. Results and Discussion

2.1 Catalytic activity of SBA-15 and Cr-SBA-15

The catalytic activity of SBA-15 was quite low. The values for isobutane conversion, selectivity for isobutene, and isobutene yield were 3.8, 36.8, and 1.4% after 0.5 h on-stream, and 3.6, 33.4, and 1.2% after 6 h on-stream, respectively. Although the selectivity of SBA-15 for isobutene was evidently greater than that of either FSM-16 or MCM-41 (8.8 and 11.2% after 6 h on-stream, respectively) (Sugiyama *et al.*, 2015; Ehiro *et al.*, 2016b), isobutene yields of these mesoporous silicas were similar (1.2% for SBA-15, 1.3% for FSM-16, and 0.9% for MCM-41 after 6 h on-stream). The introduction of chromium into SBA-15 resulted in an enhancement in the yield of isobutene to more than 15%, which has not been previously observed for the ODH of isobutane when using various solid catalysts, as shown in **Figure 1**. Increases in chromium loading from Si/Cr = 1,000 to Si/Cr = 50 resulted in enhanced isobutene conversion, but the selectivities for isobutene and CO₂ were somewhat insensitive to the Si/Cr ratio. Furthermore, the selectivities for CO and C₃ species (26.3% at Si/Cr = 1,000 and 8.4% at Si/Cr = 50, both after 0.75 h on-stream; not shown in Figure 1) increased and decreased, respectively, with increased chromium loading. Therefore, the chromium species on the catalyst directly contributed to the ODH to CO but not to the cracking of isobutane to C₃ species. It should be noted that an increase in the conversion of hydrocarbons during ODH generally results in an increase in CO₂ and a decrease in the DH product. This behavior indicates that a trade-off relationship exists between the selectivity for CO₂ and that for the DH product. As conversion and selectivity for CO₂ are generally correlated, the contribution of an active species in the catalyst toward alkane activation, which is the conversion, and the conversion to CO₂, which is the selectivity for CO₂, could be similar. In contrast, in the present study, a trade-off relationship was observed between the selectivity for CO and that for C₃ species, probably owing to the suppressed conversion of CO to CO₂. In the present study, maximum isobutene yields of more than 15% were detected using Cr-SBA-15 (Si/Cr = 100 and 50) during the initial 2.0 and 3.25 h on-stream, respectively, under the standard reaction conditions used in our previous studies (Sugiyama *et al.*, 2013, 2015; Ehiro *et al.*, 2015, 2016a, 2016b, 2017), in which the maximum isobutene yield was less than 8%. Additional activity testing using Cr-SBA-15 (Si/Cr = 50) also showed enhanced isobutene yields (16.8 and 15.3% after 0.75 and 2.0 h on-stream, respectively), which were comparable to the above yields. It is

noteworthy that CO and CO₂ were produced at a loading of Si/Cr = 1,000 for a conversion rate of less than 5%. This result may indicate that the parallel reactions shown in Eqs. (2) and (3) proceed simultaneously with the present ODH (Eq. (1)), as suggested by Neetika *et al.* (2014) for the ODH of n-butane.



2.2 Structural properties of SBA-15 and Cr-SBA-15

Table 1 shows the chromium loading, specific surface areas, pore volumes, and pore sizes of SBA-15 and Cr-SBA-15. The loading of chromium in some catalysts was estimated using ICP-AES. Chromium species were detected in all the catalysts, and the reliable loadings are described in Table 1. The BET specific surface area, pore volume, and pore size of SBA-15 (690 m²/g, 1.03 cm³/g, and 6.0 nm, respectively) were similar to those previously reported (Zhao *et al.*, 1998; Grieken *et al.*, 2009). It is noteworthy that the specific surface area of Cr-SBA-15 was enhanced with as the loading of chromium increased, reaching 1,610 m²/g in Cr-SBA-15 (Si/Cr = 50), for which the maximum activity was detected. The direct synthesis method used to prepare Cr-SBA-15 can introduce chromium species into the framework of SBA-15 (Grieken *et al.*, 2009). The introduction of a trace amount of chromium species into the SBA-15 framework resulted in a significant enhancement of the BET specific surface area, likely owing to the presence of micropores. Therefore, it is reasonable that similar

activity enhancement was not observed on supported catalysts such as CrOx/SBA-15 (Wang *et al.*, 2009).

Table 1 Chromium loading, specific surface areas, pore volumes, and pore sizes of SBA-15 and Cr-SBA-15

| Cr-SBA-15 Atomic ratio of Si/Cr | Cr [wt%] | S _{BET} [m ² /g] | S _{micro} [m ² /g] | Pore volume [cm ³ /g] | Pore size [nm] |
|---------------------------------|----------|--------------------------------------|--|----------------------------------|----------------|
| Cr = 0 | Cr = 0 | 690 | 440 | 1.03 | 6.0 |
| 1000 | — | 734 | 557 | 0.94 | 5.1 |
| 750 | — | 633 | 508 | 0.58 | 3.7 |
| 500 | 0.18 | 908 | 669 | 0.77 | 3.4 |
| 250 | 0.37 | 899 | 719 | 0.96 | 4.3 |
| 100 | — | 1356 | 1021 | 1.53 | 4.5 |
| 50 | 1.84 | 1610 | 1255 | 1.93 | 4.8 |

As shown in Table 1, there is an evident enhancement of the micropore specific surface area by the introduction of chromium. This change may indicate that the chromium species are favorably introduced into micropores rather than mesopores, which induces some strain, leading to the enhancement of the surface area.

All the N₂ adsorption-desorption isotherms could be classified as type IV (not shown). As shown in Figure 2, sharp adsorption-desorption behavior was observed for SBA-15 and Cr-SBA-15 (Si/Cr = 50) at P/P₀ of ca. 0 and 0.7, respectively, corresponding to the contribution from micro- and mesopores. The introduction of chromium SBA-15 (Si/Cr = 50) resulted

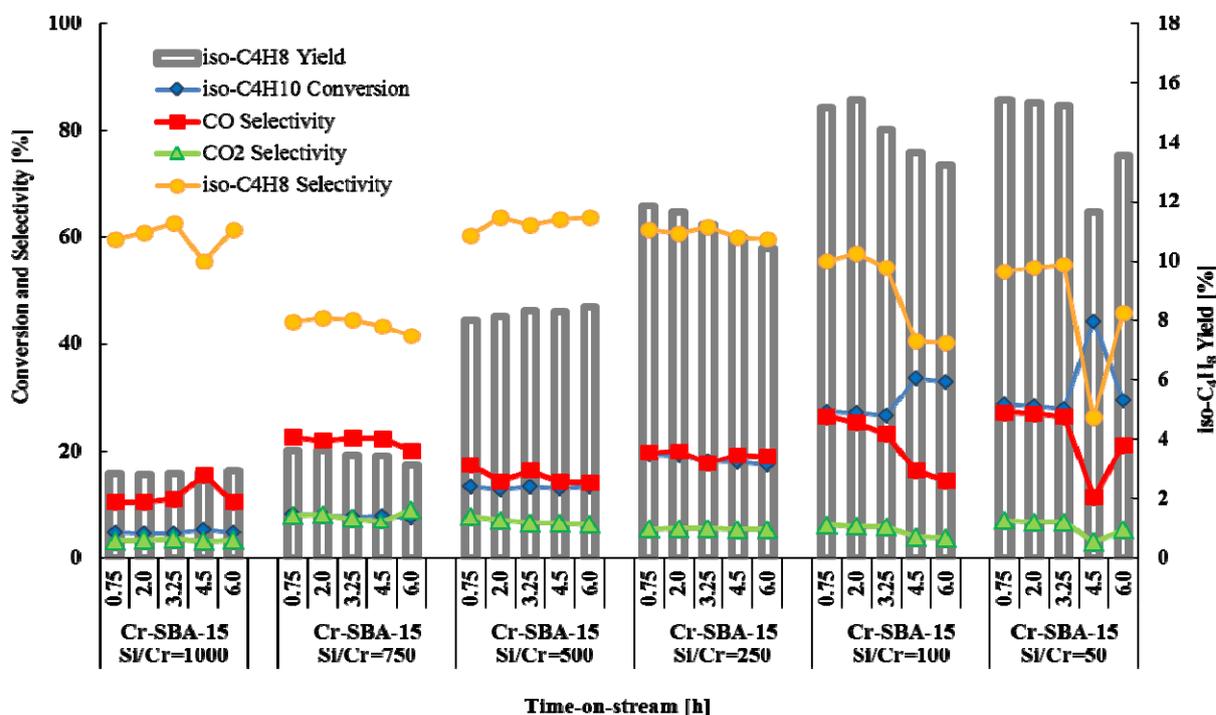


Fig. 1 Catalytic activity on various Cr-SBA-15 for the ODH of isobutane at 723 K

in a ca. three-fold enhancement in the contribution of the micropores of SBA-15, but an enhancement of mesopores was not evident, as shown in Figure 2. Therefore, the characteristic contribution of micropores corresponding to the introduction of chromium seemed to enhance the surface area of Cr-SBA-15 to 1,610 m²/g, which resulted in improved catalytic activity. This behavior is supported by the S_{micro} values listed in Table 1. It should be noted that enhancement of the specific surface area improved the contact between the reactant and the catalyst, and also improved the dispersion of chromium species in the framework of SBA-15, all of which contributed to an enhancement of the catalytic activity.

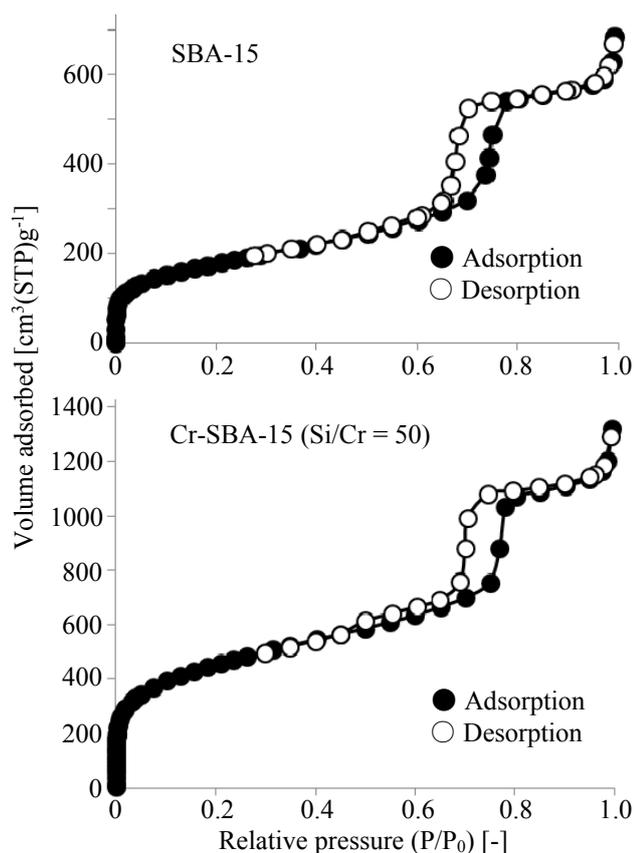


Fig. 2 N₂ adsorption-desorption isotherms of SBA-15 and Cr-SBA-15 (Si/Cr = 50)

Cr-SBA-15 (Si/Cr = 100) and Cr-SBA-15 (Si/Cr = 50) both showed excellent catalytic activities, with increased isobutene yield of greater than 15%. These catalysts, together with SBA-15, were analyzed by TEM to confirm their hexagonal structures. As shown in **Figure 3**, SBA-15 exhibited a hexagonal structure, mesopores regardless of the presence or absence of chromium.

XRD afforded additional information about the hexagonal structure of SBA-15 (**Figure 4**). Although our XRD apparatus could not detect a peak at ca. 0°, two peaks corresponding to the (110) and (200) planes between 1.5° and 2° were evident for SBA-15, as

expected (Zhao *et al.*, 1998). However, broader XRD signals were detected for Cr-SBA-15 (Si/Cr = 100) at ca. 2°. Based on the TEM results, these broader signals may originate from the hexagonal structure of Cr-SBA-15 (Si/Cr = 100), which was greatly influenced by the introduction of chromium into SBA-15. Although it is possible that chromium introduced into SBA-15 could form Cr₂O₃, no peaks corresponding to Cr₂O₃ or any other species were detected at higher diffraction angles between 10° and 60° (not shown). The XRD patterns of Cr-SBA-15 (Si/Cr = 100 and 50) before and after the reaction were essentially identical (not shown). However, after the reaction, the BET specific surface areas of Cr-SBA-15 (Si/Cr = 100 and 50) were 797 and 808 m²/g, respectively. Therefore, the decrease in the specific surface area during the reaction resulted in a decreased catalytic activity on each both catalyst after 6 h on-stream, as shown in Figure 1.

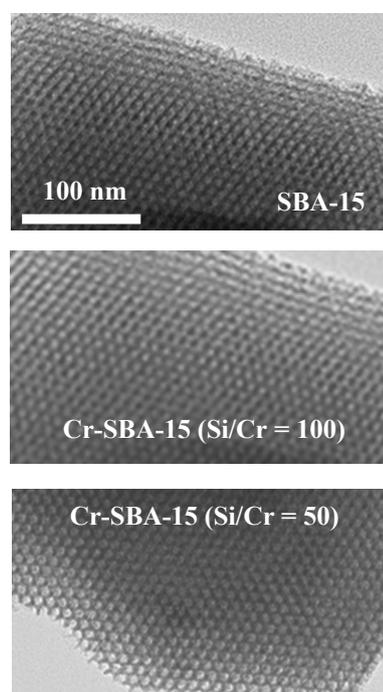


Fig. 3 TEM images of SBA-15, Cr-SBA-15 (Si/Cr = 100), and Cr-SBA-15 (Si/Cr = 50) on the same scale

In our previous studies on the ODH of isobutane using FSM-16 and MCM-41 with introduced chromium, newly formed acidic sites on the chromium-introduced mesoporous silicas contributed to enhancements in the isobutene yields (Sugiyama *et al.*, 2013, 2015; Ehiro *et al.*, 2015, 2016a, 2016b, 2017). Therefore, NH₃-TPD was used to estimate the acidic nature of Cr-SBA-15 (Si/Cr = 500, 250, and 50). However, desorption of NH₃ was not evident with these three forms of Cr-SBA-15, and only trace acidity was estimated: 0.042, 0.066, and 0.058 mmol/g (Si/Cr = 500, 250, and 50, respectively). This result indicates that Cr-SBA-15 has only a few acidic sites that were detectable by NH₃-TPD. It should

be noted that the lack of such acidic sites may not indicate that none exist, as strong acidic sites that cannot be detected using NH_3 -TPD have been observed by solid-state ^1H MAS NMR (Baba *et al.*, 1996, 1998).

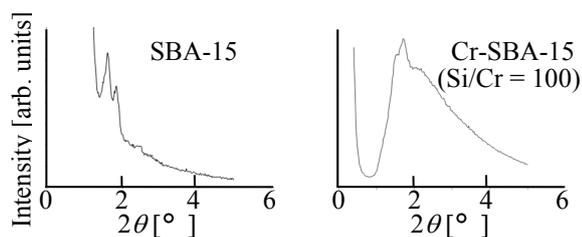


Fig. 4 XRD of SBA-15 and Cr-SBA-15 (Si/Cr = 100) at low diffraction

2.3 Factors contributing to enhanced catalytic activity of Cr-SBA-15

To explain the significant enhancement in the yield of isobutene, structural and chemical factors must be considered. Firstly, we compared the catalytic properties via a kinetic study. We assumed that isobutane was consumed in a first-order reaction and calculated the reaction rate constant (k_{i-C4}). In this estimation, the gas-space velocity was calculated using the bulk density of SBA-15 (0.210 g/mL), as measured in our laboratory. As shown in Figure 2, the introduction of chromium into SBA-15 influenced the micropores of SBA-15, and the contribution of mesopores to the reaction rate constant was examined. The $k_{i-C4}/S_{\text{micro}}$ values show the reaction rate constant per surface area of micropores of Cr-SBA-15, and these values are summarized in **Table 2**. The catalyst that had the greatest micropore surface area showed the greatest reaction rate constant. To the best of our knowledge, such behavior has not been observed in any other mesoporous silicas. Therefore, the reaction field formed via the synergistic effect of meso- and micropores resulted in an enhancement of the reaction constant. The amount of chromium affected the catalytic activity when the loading was less than 0.37 wt% (Si/Cr = 250). However, further loading of chromium only had a small influence on the activity, as shown in Figure 1. It is noteworthy that the enhanced activity of Cr-SBA-15 (Si/Cr = 100 and 50) seemed to be correlated with the surface area.

With respect to the structural factors, a specific surface area of greater than 1,600 m^2/g should be a main contributor to enhanced activity. The growth of micropores in Cr-SBA-15 was detected in the present study, but this feature has not been observed in either FSM-16 or MCM-41 when doped with chromium (Sugiyama *et al.*, 2013, 2015; Ehiro *et al.*, 2015, 2016a, 2016b, 2017). Therefore, this structural factor is unique to Cr-SBA-15 and results in increased activity.

We focused on examining chromium species in Cr-SBA-15, and according to our and previous reports, reducible Cr^{6+} species in Cr-MCM-41 contributed to improvements in the catalytic activity (Ehiro *et al.*, 2016a; Wang *et al.*, 2009). As shown in Table 2, it is

noteworthy that $k_{i-C4}/S_{\text{micro}}$ increased as the chromium loading increased from Cr = 0 to Si/Cr = 1,000 to Si/Cr = 250, with different trends observed at Si/Cr ratios smaller than Si/Cr = 250. Therefore, the surface situation of chromium species, such as Cr^{6+} or Cr^{3+} , may be significantly changed at a loading of Si/Cr = 250. As shown in Figure 2, the behaviors of isobutane conversion and the selectivity for each product following chromium loading were rather different from those on general solid catalysts. It is reasonable that Cr^{6+} species are easily formed at lower chromium loadings, whereas increased chromium loading results in the increased formation of Cr^{3+} species together with Cr^{6+} species. An excess loading of chromium species may result in the sole formation of Cr^{3+} species without any Cr^{6+} species. Therefore, the balance between Cr^{6+} species and the original Cr^{3+} species, which could change the catalytic activity at approximately Si/Cr = 250, could be a critical factor in the present system. However, the quantities of chromium species were too low to be detected using X-ray photoelectron spectroscopy (XPS). Although there is no empirical evidence for differences in chromium species, there is a possibility that both the presence of Cr^{6+} species and the greater surface area may contribute to the enhanced isobutene yield, which has yet to be reported using other mesoporous silicas.

Table 2 Reaction rate constants and reaction rate constants per surface area with respect to chromium loading

| Cr-SBA-15 Atomic ratio of Si/Cr | Cr [wt%] | k_{i-C4} [1/s] | $k_{i-C4}/S_{\text{micro}} \times 1000$ [$\text{g}/\text{m}^2 \cdot \text{s}$] |
|---------------------------------|----------|------------------|--|
| Cr = 0 | Cr = 0 | 0.0081 | 0.0185 |
| 1000 | — | 0.0099 | 0.0178 |
| 750 | — | 0.0178 | 0.0350 |
| 500 | 0.18 | 0.0288 | 0.0431 |
| 250 | 0.37 | 0.0448 | 0.0624 |
| 100 | — | 0.0665 | 0.0651 |
| 50 | 1.84 | 0.0700 | 0.0558 |

Conclusions

During the ODH of isobutane to isobutene, the catalytic activity was dramatically improved when using SBA-15 with a small amount of incorporated chromium. As the maximum isobutene yield when using chromium-incorporated FSM-16 and MCM-41 were only 8%, a significant improvement in yield (>15%) was achieved by using Cr-SBA-15. One of the factors possibly responsible for this enhancement was a Cr^{6+} species, which was undetectable using XPS in the present study. Another factor was the optimal specific surface area of the catalyst, which was gained via the introduction of chromium into the framework of SBA-15.

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