

Effect of Introduction of Trace Amount of Chromium Species in Improving Catalytic Performance of MCM-48 in Oxidative Dehydrogenation of Isobutane

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The catalytic performance of MCM-48 was greatly improved by the introduction of a small amount of chromium during the oxidative dehydrogenation of isobutane. Various characterization procedures such as XRD, N₂ adsorption-desorption isotherms, TEM, NH₃-TPD, XPS, and XAFS were used to identify the role that chromium played in the improvement, and XPS and XAFS results provided the most valuable information. Both measurements revealed that the chromium species existed as Cr⁶⁺ inside the framework of MCM-48 before oxidative dehydrogenation, but was reduced to Cr³⁺ during the reaction. The characteristic pore nature of MCM-48 also contributed to an enhancement of the selectivity to isobutene via the suppression of consecutive oxidation reactions.

Introduction

Methyl methacrylate (MMA) is an important monomer of poly(methyl methacrylate) and functional chemicals for films, coatings, paints and so on. Herein, we focus on the process of C₄ direct oxidation from among the various production routes to MMA (Ninomiya *et al.*, 2014). In this process, MMA is produced from isobutene or tert-butanol (TBA). Isobutene, however, is supplied from ethylene and fluid catalytic cracking (FCC) plants via a supply route that is undoubtedly insufficient (Nagai, 2001). Therefore, the development of a new route for the production of isobutene is desired. Under these circumstances, oxidative dehydrogenation (ODH) and dehydrogenation (DH) of isobutane to isobutene have been investigated. Some laboratories (Ohta *et al.*, 2004; Airaksinen *et al.*, 2005; Korhonen *et al.*, 2007) have focused exclusively on the DH of isobutane to determine various candidate catalysts. Unfortunately, DH is an endothermic reaction that requires high reaction temperatures that often result in rapid deactivation of catalysts. On the other hand, ODH is an exothermic reaction that can be performed at a reaction temperature that is lower than that required for DH. It is difficult to improve the selectivity to isobutene, however, due to the immediate conversion of

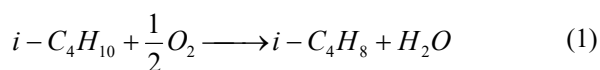
isobutene to CO₂ via consecutive oxidation. In our laboratory, various metal oxides have been investigated as catalysts for ODH under coexistence with gaseous oxygen. The use of gaseous oxygen suppresses the deposition of coke over the catalyst. We first examined the ODH of isobutane (Eq. (1)) using various complex metal oxide catalysts such as magnesium vanadates and magnesium molybdates. However, the yield of isobutene was insufficient (less than 2%) when obtained at reaction temperatures sufficiently low (<723 K) to suppress the homogeneous oxidation of isobutane (Furukawa *et al.*, 2011). On the other hand, various chromium-introduced solid oxide catalysts have been suggested as possible candidates for the DH and ODH of isobutane (Moriceau *et al.*, 2000; Jibril *et al.*, 2005; Wang *et al.*, 2009). Therefore, introduction of the chromium species into various mesoporous silicas and its effect on the ODH of isobutane has remained a research focus in our laboratory, and we found that the catalyst performance was enhanced (Sugiyama *et al.*, 2015). For example, the chromium species was either introduced or impregnated into various mesoporous silica catalysts possessing a uniform hexagonal structure such as FSM-16 (Sugiyama *et al.*, 2013, 2015; Ehiro *et al.*, 2015) and MCM-41 (Ehiro *et al.*, 2016a, 2016b) and great improvement in the yield of isobutene was recorded ($\approx 8\%$ at 723 K). Recently, a similar enhancement was observed during the ODH of isobutane using SBA-15 when a trace amount of chromium was introduced (Kato *et al.*, 2018). In that study, however, the chromium species could not be

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characterized due to its small amount. Furthermore, it was unclear if the enhancement by chromium would be observed with other mesoporous silicas, particularly those possessing a non-hexagonal structure. In the present study, MCM-48 was employed as a mesoporous silica catalyst with a non-hexagonal structure. MCM-48 has a high degree of surface area and a three-dimensional pore structure (Brett *et al.*, 2007). Compared with FSM-16, MCM-41, and SBA-15, we expected MCM-48 to deliver greater catalytic performances with regards to activity, selectivity to isobutene, and resistance to deactivation, because all those previous catalysts possess a uniform hexagonal structure. The three-dimensional pore structure of MCM-48 was expected to also contribute to more favorable diffusion of the reactants and products as the structure is highly resistant to pore blockage (Schumacher *et al.*, 2000). To introduce chromium into the framework of mesoporous silica, one of two methods is generally applied the direct synthesis method (Grieken *et al.*, 2009) and template ion exchange (TIE) method (Yonemitsu *et al.*, 1997). The direct synthesis method has sometimes been used to introduce chromium into MCM-48, which revealed that the surface area of MCM-48 decreased with the introduction of increasing amounts of chromium (Yaofeng *et al.*, 2008; Lingzhi *et al.*, 2009). The TIE method has been used to introduce various cations, such as manganese, other than chromium into MCM-48, and with this method the MCM-48 was able to maintain a greater surface area (Ioana *et al.*, 2011). Therefore, in the present study, the ODH of isobutane to isobutene was examined using MCM-48 introduced with chromium via the TIE method, and the catalytic activity was characterized via XRD, XPS, TEM, N₂ adsorption-desorption isotherms, NH₃-TPD, and XAFS. In particular, we focused on characterizing and discussing the addition of a small amount of chromium, using XPS and XAFS measurements.



1. Experimental

1.1 Synthesis of catalysts

MCM-48 was prepared as reported by Brett *et al.* (2007). Cetyl trimethyl ammonium bromide (CTAB) (Wako Pure Chemical Industries, Ltd.) (8.97 g) was added to distilled water (371.82 g) and stirred at 300 rpm for 5 min at room temperature. Ethanol (Wako Pure Chemical Industries, Ltd.) (147.24 g) was added to the solution with stirring at 300 rpm for 5 min at room temperature. Then, 28 wt% NH₃ aq. (Wako Pure Chemical Industries, Ltd.) was added and stirred at 300 rpm for 5 min at room temperature. Additionally, tetraethylorthosilicate (TEOS) (Shin-Etsu Chemical Co., Ltd.) (12.50 g) was added with stirring at 300 rpm for 4 h at room temperature. The precipitate was recovered by

filtration and washed with 600 mL of distilled water and then dried at 332 K for 2 days. A white powder was obtained and denoted as "As-synthesized MCM-48." Finally, MCM-48 was obtained by calcination at 823 K for 6 h (heating rate = 1 K/min). Chromium was introduced via the TIE method reported by Yonemitsu *et al.* (1997). As-synthesized MCM-48 (3.0 g) was dispersed in distilled water (30 mL) and stirred at 350 rpm. A chromium solution was obtained from the dissolution of Cr(NO₃)₃·9H₂O (Sigma-Aldrich Co. LLC.) into distilled water (30 mL) and added slowly with additional stirring for 1 h under the same conditions. The obtained mixture was kept at 353 K for 20 h without stirring. When a solid was recovered by filtration, it was washed with distilled water and allowed to dry at 332 K for a day. Finally, MCM-48 with chromium was obtained following calcination at 823 K for 6 h (heating rate = 1 K/min). The MCM-48 with chromium was denoted as "Cr-MCM-48." The amount of chromium introduced in Cr-MCM-48 was controlled via the concentration of the chromium solution to atomic ratios of Si/Cr = 10,000; 1,000; 100; or 40. These catalysts are denoted as "Cr-MCM-48 (Si/Cr ratios = 10,000; 1,000; 100; or 40)." The atomic ratios of the all catalysts were confirmed via ICP-AES (SPS3520UV, SII Nanotechnology Inc.).

1.2 Characterization of catalysts

The structural details of the catalysts were obtained via X-ray diffraction (XRD; SmartLab/RA/INP/DX, Rigaku Co.), N₂ adsorption-desorption isotherm measurement (BELSORP-max12, MicrotracBEL), and transmission electron microscopic examination (TEM; JEM-2100F, JEOL Ltd.). Monochromatized Cu K α radiation (45 kV, 150 mA) was used for the XRD analysis. N₂ adsorption-desorption isotherm was obtained at 77 K after the pre-treatment of the catalysts at 473 K for 5 hours under vacuum. The obtained isotherms were analyzed using a BET equation and the BJH method to measure the surface area, pore diameter, and pore volume of each catalyst. The acidic properties of the catalysts were measured using NH₃ temperature-programmed desorption (NH₃-TPD; BELCAT, MicrotracBEL). Following pre-treatment of the catalysts under 50 sccm of He gas flow at 773 K for 1 h followed by maintenance at 373 K for 10 min, the main treatment with NH₃ adsorption was carried out under 50 sccm of 5 % NH₃/He gas flow for 30 min. After the main treatment, the catalyst was maintained under less than 50 sccm of He gas for 15 min and was then heated from 373 K to 883 K (heating rate = 10 K/min) under 30 sccm of He gas flow. Desorbed NH₃ from the catalyst was detected using a quadrupole mass spectrometer (BELMass, MicrotracBEL) that monitored a mass signal of m/e = 16 for NH₃. The surface property of the catalysts was estimated using XPS (PHI-5000VersaProbe II, ULVAC-PHI Inc.). The XPS

spectra were calibrated based on the C 1s peak at 285.0 eV. The fine-structure changes around the chromium species in the catalysts were estimated using XAFS measurement carried out using synchrotron radiation from the BL9A station at the Photon Factory of the High Energy Accelerator Research Organization (Tsukuba, Japan). The storage ring energy and current were 2.5 GeV and 450 mA, respectively. The X-rays were monochromatized using a Si(111) water-cooled double crystal.

1.3 Testing of catalytic performances

Testing of catalytic performances was carried out with a fixed-bed continuous flow reactor under atmospheric pressure at 723 K. Each catalyst (0.25 g) was pelletized and sieved to 0.851.70 mm. Then, each obtained catalyst was fixed with quartz wool into each reactor. After the pre-treatment of catalysts under 12.5 mL/min of O₂ gas flow at 723 K for 1 h, testing of catalytic performances was started under 15 mL/min of a reactant gas flow that consisted of He, O₂, and isobutane. The partial pressures of the reactant gases were adjusted to $P(\text{He}) = 74.6$ kPa, $P(\text{O}_2) = 12.3$ kPa, and $P(\text{isobutane}) = 14.4$ kPa respectively. No homogeneous reaction was detected under these conditions. The reaction products were monitored using an on-line gas chromatograph (GC-8APT, Shimadzu Corp.) equipped with a thermal conductivity detector (TCD) and a capillary gas chromatograph (GC-2025, Shimadzu Corp.) equipped with a flame ionization detector (FID). The columns used in TCD-GC included a Molecular Sieve 5A (0.2 m×Φ3 mm) for O₂, CH₄ and CO and a HayeSep R (2.0 m×Φ3 mm) for CO₂, C₂, C₃ and C₄ products. The C₄ species were further confirmed using an Rt-Alumina BOND/Na₂SO₄ capillary column (30 m×Φ0.53 mm). The carbon balance between the reactant and the product gases was within ±5%.

Catalytic performances such as the selectivity to each product and the conversion of isobutane were calculated on a carbon basis.

2. Results and Discussion

2.1 Catalytic performance of MCM-48 and Cr-MCM-48

Figure 1 shows the catalytic performances for MCM-48 and Cr-MCM-48 (Si/Cr ratios = 10,000; 1,000; 100; and 40). Over MCM-48, isobutane was barely converted, as with other mesoporous materials such as FSM-16 and MCM-41 (the yields of isobutene were 1.9% for MCM-48, 1.3% for FSM-16, 0.9% for MCM-41, and 3.6% for SBA-15 at 6 h on-stream) (Sugiyama et al., 2015; Ehiro et al., 2016b; Kato et al., 2018). The conversion of isobutane and the selectivity to isobutene were greatly improved by introducing only a small amount of chromium into MCM-48. As shown in Figure. 1, the conversion of isobutane was increased when the amount of chromium introduced increased to a Si/Cr ratio = 1,000, and gradually decreased as the amount of introduced chromium was increased. The selectivity to isobutene was almost independent of the Si/Cr ratio. In contrast, the selectivity to CO_x increased as the amount of chromium introduced increased to a Si/Cr ratio = 100, which was similar to the conversion of isobutane. As a result, a maximum yield of isobutene greater than 7.0% resulted when using Cr-MCM-48 at a Si/Cr ratio = 1,000. It should be noted that improvement in the yield of isobutene was most significant for a Si/Cr ratio = 1,000.

2.2 Characterizations of pure-MCM-48 and Cr-MCM-48

Structural properties of the catalysts were analyzed using with N₂ adsorption-desorption isotherms, XRD, and TEM. Figure 2 shows the N₂ adsorption/desorption

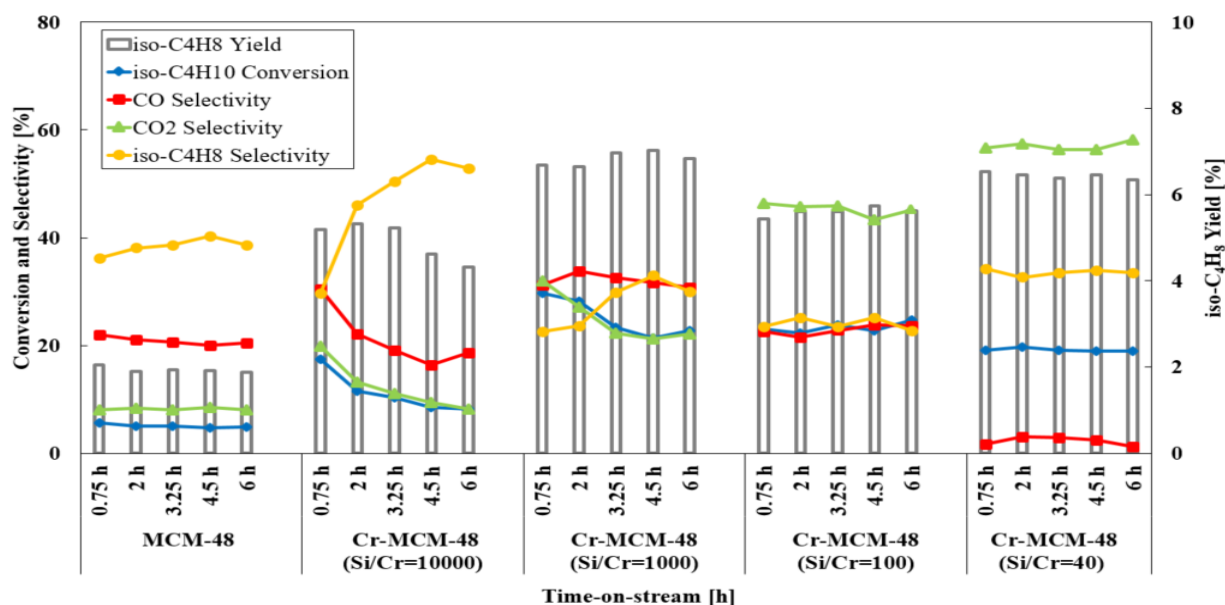


Fig. 1 Catalytic activity on various Cr-MCM-48 for the ODH of isobutane at 723 K.

isotherms of all the catalysts. All isotherms were categorized as type IV, and the isotherms showed the characteristic shape for capillary condensation in a mesopore at $p/p_0 = 0.20.3$. Hysteresis was not observed.

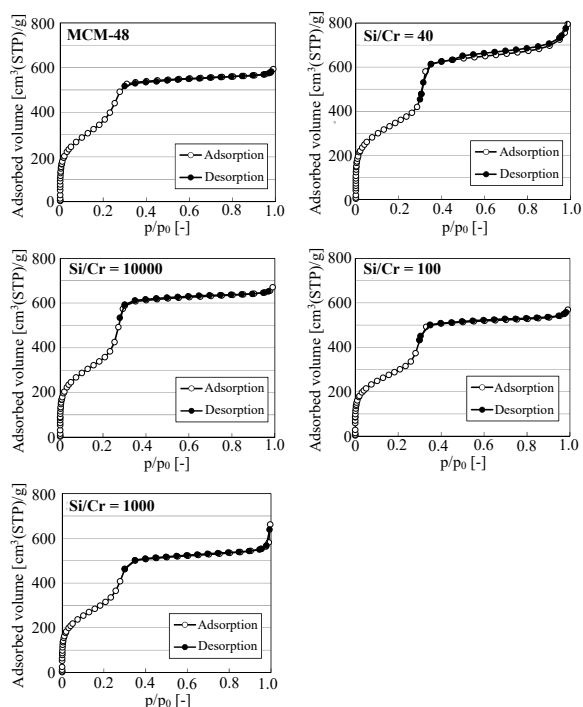


Fig. 2 Nitrogen adsorption-desorption isotherms at 77 K of pure MCM-48 and Cr-MCM-48 (Si/Cr ratios = 10,000; 1,000; 100; and 40).

Table 1 Amount of chromium introduced, surface area, pore volume, and pore size of MCM-48 and Cr-MCM-48.

| Cr-MCM-48 | Cr | S_{BET} | Pore volume | Pore size |
|-----------------------|--------|-------------|--------------|-----------|
| Atomic ratio of Si/Cr | [wt%] | [m^2/g] | [cm^3/g] | [nm] |
| Cr = 0 | Cr = 0 | 1307 | 0.92 | 2.81 |
| 10000 | 0.014 | 1260 | 1.03 | 3.29 |
| 1000 | 0.15 | 1116 | 0.91 | 3.25 |
| 100 | 1.19 | 1070 | 0.88 | 3.28 |
| 40 | 2.72 | 1070 | 0.88 | 3.28 |

Table 1 shows the chromium content of MCM-48 and Cr-MCM-48 estimated using ICP-AES, surface areas, pore volumes and pore sizes. The surface area of MCM-48 (1,307 m^2/g) was greater than that of other mesoporous materials such as FSM-16, MCM-41, and SBA-15 (871, 788, and 690 m^2/g , respectively) (Ehiro et al., 2015, 2016a, 2016b; Kato et al., 2018). This larger surface area was observed in each example of Cr-MCM-48, and decreased when the amounts of chromium were increased. The pore sizes of Cr-MCM-48 were consistent regardless of the amount of chromium while

the pore size was evidently greater than that in MCM-48.

Figure 3 shows the XRD patterns within a low diffraction angle range ($2.0 < 2\theta < 6.0$) of MCM-48 and Cr-MCM-48. The patterns of MCM-48 and Cr-MCM-48 (Si/Cr ratio = 10,000) exhibited diffraction due to (211) and (220) planes, which are categorized as the space group Ia3d that provides a three-dimensional pore structure (Beck et al., 1992). The pattern of Cr-MCM-48 (Si/Cr ratios = 1,000; 100; and 40) exhibited (100), (110), and (200) planes, which correspond to a two-dimensional hexagonal structure for mesoporous materials such as FSM-16, MCM-41, and SBA-15 (Inagaki et al., 1996; Beck et al., 1992; Zhao et al., 1998). Additionally, these patterns were shifted to a lower angle as increasing amounts of chromium were introduced. No peaks due to Cr_2O_3 or any other chromium species were detected with a greater diffraction angle ($10 < 2\theta < 60$) (not shown).

Figure 4 shows the TEM images of Cr-MCM-48 (Si/Cr ratios = 1,000 and 100). A highly ordered mesoporous structure was observed with no particles of chromium species. Therefore, Cr-MCM-48 should be a highly ordered mesoporous structure with highly dispersed chromium species. Based on the structural properties listed above, the amount of chromium species that we considered as active species increased, resulting in positive effects for improvement of the catalytic activity. In contrast, the specific surface area decreased with the introduction of chromium, resulting in negative effects. Therefore, the best conversion for isobutane was achieved at a Si/Cr ratio = 1,000 because of the balance between the positive effects and the negative effects. Enhancement of the catalytic performance by introducing chromium was observed regardless of whether the pore structure was two-dimensional and hexagonal or three-dimensional. Therefore, the specific surface area strongly influences the conversion for isobutane. However, the most advantageous structures may be the three-dimensional version, which is discussed later.

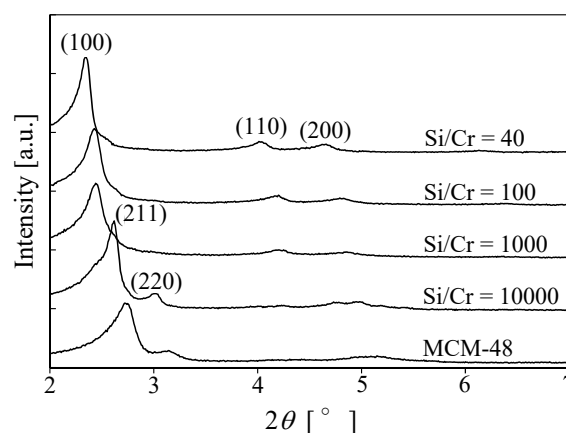


Fig. 3 XRD patterns of MCM-48 and Cr-MCM-48 (Si/Cr ratios = 10,000; 1,000; 100; and 40).

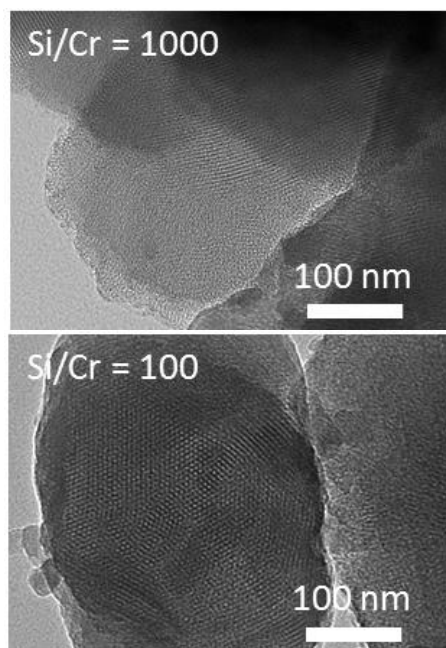


Fig. 4 TEM images of Cr-MCM-48 (Si/Cr ratios = 1,000 and 100).

The acidic properties of MCM-48 and Cr-MCM-48 were examined using NH_3 -TPD. **Figure 5** shows the NH_3 -TPD spectra of MCM-48 and Cr-MCM-48. Almost no peaks were detected from either MCM-48 or Cr-MCM-48 with Si/Cr ratios = 10,000 and 1,000. Two broad peaks at approximately 548 K and 664 K were observed for Cr-MCM-48 with Si/Cr ratios = 100 and 40, and the intensity of the peaks increased as greater amounts of chromium were introduced. In our previous report (Ehiro *et al.*, 2016a), we suggested that the acidic sites for NH_3 desorption peak at approximately 565 K corresponded to the active sites for the ODH reaction of isobutane. In the present report, the improvement of the catalytic performance of MCM-48 with chromium could be attributed to the acidic sites. However, the real effect of the acidic sites on the enhancement of the catalytic performance remained unclear because the effect of the increase in the amount of chromium on the number of the acidic sites and the specific surface area were completely reversed, which suggests that an increase in the amount of chromium was advantageous for increasing the acidic sites but not for the surface area.

Finally, the chemical properties and redox nature of the chromium in Cr-MCM-48 were examined using XPS and XAFS. Cr-MCM-48 with Si/Cr ratios = 1,000 and 100 were used for measurement. **Figure 6** shows the XPS spectra for Cr 2p of Cr-MCM-48 with a Si/Cr ratio = 100 before and after the reaction. Unfortunately these data were not obtained for Cr-MCM-48 with a Si/Cr ratio = 1,000 due to the limited amount of chromium species. Chromium species in Cr-MCM-48 with Si/Cr = 100 could not be characterized due to the low intensity of spectra, while the existence of chromium species was detected. In order to obtain clearer evidence for the presence of Cr^{6+} and/or Cr^{3+} ,

XAFS was employed for both catalysts. **Figure 7** shows the Cr K-edge XANES spectra of Cr_2O_3 and Cr-MCM-48 with Si/Cr ratios = 1,000 and 100 before and after the reaction. Chromium species from both Cr-MCM-48 were finally detected. The XANES spectra of both samples of Cr-MCM-48 before the reaction showed pre-edge absorption at ca. 5,990 eV, which indicated that the chromium species possesses a tetrahedral coordination structure that consists of the Cr^{6+} species (Chanho and Haller, 2001). After the reaction, the absorption peak was shifted by ca. 3.6 eV to a lower level of energy, while the pre-edge absorption peak disappeared. The XANES spectra of the catalysts after the reaction were similar to that of Cr_2O_3 , indicating that the chromium species had an octahedrally coordinated structure. These details revealed that the structure of chromium species changed from tetrahedral to octahedral coordination, while the chromium species was reduced from Cr^{6+} to Cr^{3+} during the reaction. It should be noted, however, that the valences of Cr-MCM-48 after the reactions were almost 3+.

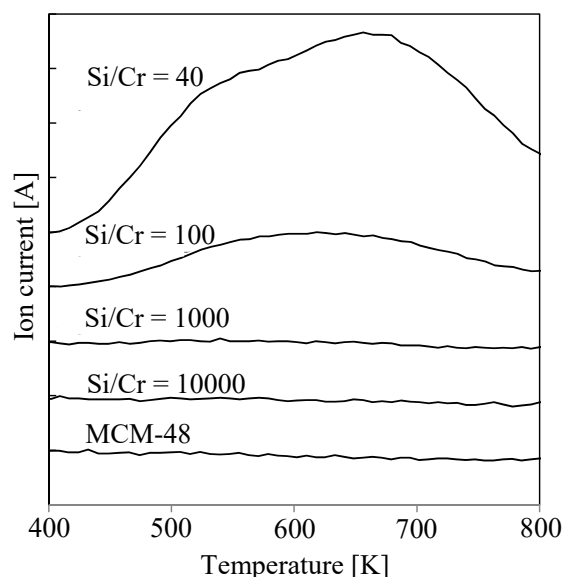


Fig. 5 NH_3 -TPD spectra of MCM-48 and Cr-MCM-48 (Si/Cr ratios = 10,000; 1,000; 100; and 40)

Therefore, as shown in **Figure 8**, when synthesized as suggested by Wang *et al.* (2009), the chromium species of $\text{Cr}(\text{NO}_3)_3$ with a valence of 3+ was introduced into the framework of MCM-48 and formed linkages such as Si-O-Cr^{6+} and $\text{Cr}^{6+}\text{-O-Cr}^{6+}$ rather than crystalline Cr_2O_3 . Those Cr^{6+} species in the linkages become active sites for the ODH of isobutane, as proposed by Sugiyama *et al.* (2016) and Takita *et al.* (2005). During the ODH, isobutane is adsorbed onto the lattice oxygen to form either a bridge or a terminal oxygen that surrounds either Cr^{6+} and the linkages or only the Cr^{6+} . An isobutylcarbenium cation and H^- then forms, and isobutene is released from the isobutylcarbenium cation. The remaining H^- and H^+ on

lattice oxygen forms H₂O with lattice oxygen, which is then released. As a result, Cr⁶⁺ is reduced to Cr³⁺ but normally re-oxidized to Cr⁶⁺ by oxygen.

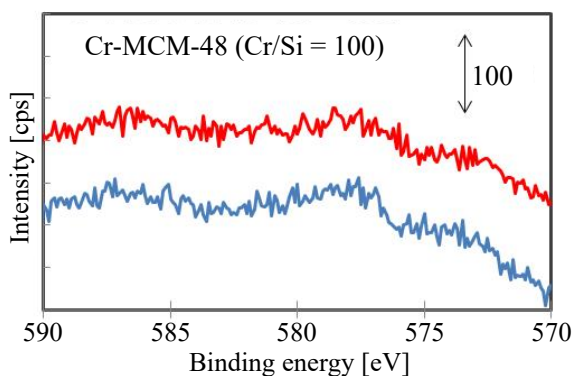


Fig. 6 XPS of Cr 2p from Cr-MCM-48 with a Si/Cr ratio = 100. The blue and red lines correspond to before and after the reaction, respectively.

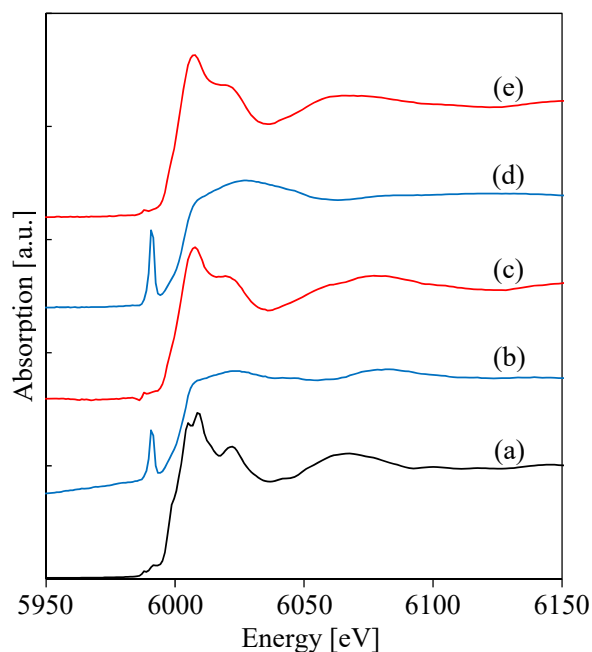


Fig. 7 Cr K-edge XAFS spectra of (a) Cr₂O₃, (b) Cr-MCM-48 with a Si/Cr ratio = 1,000 before the reaction, (c) Cr-MCM-48 with a Si/Cr ratio = 1,000 after the reaction, (d) Cr-MCM-48 with a Si/Cr ratio = 100 before the reaction, and (e) Cr-MCM-48 with a Si/Cr ratio = 100 after the reaction.

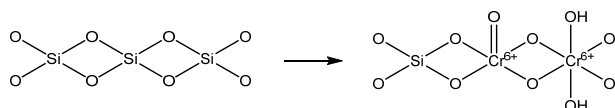
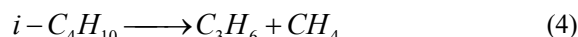
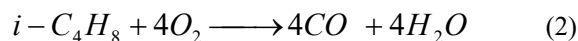


Fig. 8 Introduction of chromium into the framework of MCM-48

2.3 Contribution of the three-dimensional pore structure of MCM-48 to catalytic performance

As a result of the characterizations in the present study, the Cr-MCM-48 with a Si/Cr ratio = 10,000 was only one of the present catalysts possessing a three-dimensional pore structure. As described above, the consecutive oxidations of isobutene to CO (Eq. (2)) and CO₂ (Eq. (3)) were suppressed by the high diffusion properties inside the three-dimensional pore structure. Cr-MCM-48 with a Si/Cr ratio = 10,000 showed the greatest selectivity to isobutene from among all catalysts used in the present study. However, a discussion of only the influence of the pore structure would be insufficient because the influence of consecutive oxidations, as (Eq. (3)) reported by Hoang *et al.* (2010), and parallel reactions such as the cracking reaction that produces C₃ products, as (Eq. (4)) reported by Takita *et al.* (2005), proceeded concurrently. Therefore, in the present study we focused on the relationship between the converted amounts of isobutane and the converted amount of oxygen, as shown in **Figure 9**. If the ideal oxidative dehydrogenation of isobutane proceeded as Eq. (1) dictates, the ratio of “the converted amount of isobutane” to “the converted amount of oxygen” would fall between 1 and 0.5. The proportion of converted oxygen should be more apparent as the consecutive reaction (Eq. (2) and Eq. (3)) occurs, while the contribution of the cracking reaction would disappear, since the cracking reaction does not require oxygen.



The dotted line in Figure 9 highlights a ratio of 1 to 0.5 as the ideal ratio for the ODH reaction. MCM-48 and Cr-MCM-48 with Si/Cr ratios = 100 and 40, respectively, both appear on the line drawn using their respective data using the least squares method with a slope of approximately 3.5. The line denoting Cr-MCM-48 with a Si/Cr ratio = 10,000 had a slope ratio of 1.9, which was the lowest value among all catalysts in the present study. Therefore, the version of Cr-MCM-48 with a Si/Cr ratio = 10,000 used oxygen more efficiently during the reaction owing to a three-dimensional pore structure that suppressed consecutive oxidation and improved the gas diffusion. In contrast, the version of Cr-MCM-48 with a Si/Cr ratio = 1,000 had a slope ratio of 2.8 and no three-dimensional pore structure, but its surface area and pore volume were greater than those of the Cr-MCM-48 with Si/Cr ratios = 100 and 40, which means that Cr-MCM-48 with Si/Cr ratio = 1,000 has more efficient pore structures for gas diffusion than Cr-MCM-48 with Si/Cr ratio = 100 and 40.

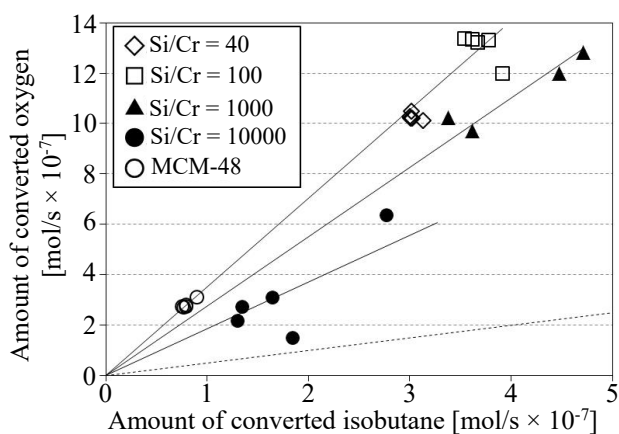


Fig. 9 The relationship between the amount of the converted isobutane and oxygen of MCM-48 and Cr-MCM-48 (Si/Cr ratios = 10,000; 1,000; 100; and 40)

Conclusions

The catalytic activity of MCM-48 was greatly improved with the introduction of chromium species. The maximum catalytic performance was detected when using Cr-MCM-48 (Si/Cr ratio = 1,000) due to the balance between the advantages and demerits of chromium introduction. At this ratio, the increase in the surface area of the catalyst was limited, but this limitation was not serious enough to offset improvements made to the pore structure. The chromium species was detectable via XPS and XAFS, and the redox properties of even a small amount of chromium contributed to the ODH reaction. The formation of a three-dimensional pore structure and increase in the surface area and pore volume all contributed to the suppression of the consecutive reactions.

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