

Modifying SBA-15 with Binary Elements of Chromium and Molybdenum for Improved Catalytic Performance in the Oxidative Dehydrogenation of Isobutane to Isobutene

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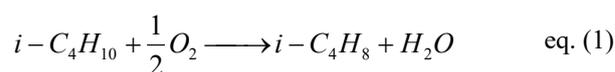
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In the oxidative dehydrogenation of isobutane to isobutene, selectivity and stability were improved by introducing chromium and molybdenum into SBA-15. The direct synthesis method (DM) was used to introduce these binary elements into SBA-15. Use of the DM resulted in a higher specific surface area of the catalyst and a greater dispersion of chromium and molybdenum species compared with a corresponding binary catalyst prepared using the incipient wetness impregnation method (IM). Selectivity to isobutene was improved, along with a decrease in the selectivities to CO and CO₂ with the introduction of greater amounts of molybdenum, which suggests that molybdenum must suppress the tendency of isobutene to over-oxidate to either CO or CO₂. The molybdenum species must be in close proximity to the chromium species, which results in the formation of an active Cr-O-Mo site.

Introduction

Methyl methacrylate (MMA) monomer is a major material in the composition of functional chemicals such as films, sheets, pellets, optical fibers, coatings and paints. Various industrial processes are used to produce MMA monomers. More than half of these are acetone cyanohydrin (ACH) processes. In Asia, however, C₄ direct oxidation is the main method (Ninomiya *et al.*, 2014). In this process, tert-butanol (TBA), or isobutene, is used as the main raw material. Since TBA is produced from isobutene, the development of a method for the production of isobutene is a key for direct C₄ oxidation. Isobutene is generally derived from ethylene via FCC (fluid catalytic cracking) processes. It is often pointed out, however, that the supply of isobutene is undoubtedly insufficient (Nagai *et al.*, 2001). Therefore, the present study was focused on the oxidative dehydrogenation (ODH) of isobutane as a potential supply of isobutene (eq. (1)). On the other hand, some laboratories (Ohta *et al.*, 2004; Airaksinen *et al.*, 2005; Korhonen *et al.*, 2007) have focused on direct dehydrogenation (DH) of isobutane to isobutene with an absence of oxygen in the reactant stream. Direct DH is an endothermic reaction, which normally requires a higher reaction temperature that results in an easy

deactivation of the catalysts due to the formation of carbon deposits. By contrast, ODH is an exothermic reaction that is conducted at a lower temperature. ODH has a serious drawback, however, because the isobutene selectivity is low. Based on earlier papers concerning the ODH of isobutane (Jibril *et al.*, 2005; Moriceau *et al.*, 2000; Wang *et al.*, 2009), our group has investigated various metal-doped meso-porous catalysts for the ODH of isobutane to isobutene and confirmed that meso-porous silica catalysts modified with chromium are suitable for this reaction (Sugiyama *et al.*, 2013, 2015; Ehiro *et al.*, 2015, 2016a, 2016b; Kato *et al.*, 2018). From a practical point of view, however, it is preferable to reduce the amount of chromium in the catalysts as much as possible due to toxicity. For this purpose, we focused on meso-porous silica catalysts modified with binary elements of chromium and another element. In the present paper, the catalytic performances of SBA-15 modified with chromium and molybdenum was examined based on preliminary experiments using binary systems.



1. Experimental section

1.1 Preparation of catalysts

Unmodified SBA-15 (SBA-15) was prepared using a method reported by Zhao *et al.* (1998). Pluronic 123 (P123) (Sigma-Aldrich Co. LLC.) (6.00 g) and KCl (Wako Pure Chemical Industries, Ltd.) (6.72 g) were

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added to a 2M HCl aqueous solution (Wako Pure Chemical Industries, Ltd.) (180 mL). Tetraethylorthosilicate (TEOS) (Shin-Etsu Chemical Co., Ltd.) (11.48g) was added to the solution, which was then stirred for 8 min. The solution was then maintained at 317 K for 24 h under static conditions. The resultant solution was reacted in an autoclave at 373 K for 24 h to achieve hydrothermal synthesis. A white precipitate was recovered via filtration after the solution was washed with distilled water and then dried at 332 K for 2 days. Finally, the resultant solid was calcined at 823 K for 6h (heating rate = 1.8 K/min) to yield SBA-15.

In order to introduce chromium and molybdenum into SBA-15, a direct synthesis method (DM) reported by Grieken *et al.* (2009) was employed. It should be noted that Cr-Modified SBA-15 via the DM showed great catalytic performance (Kato *et al.*, 2018). The chromium and/or molybdenum were introduced into SBA-15 using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich Co. LLC.) and/or $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd.) as the corresponding precursors after the addition of TEOS during the preparation of unmodified SBA-15. The amounts of Si, Cr and Mo were adjusted to achieve atomic ratios of Si:Cr:Mo = 100:0.1:0.1, 100:1:1, 100:2:2, 100:2:0, 100:0:2, 100:2/3:2, and 100:2:2/3. The resultant catalysts were designated Cr,Mo-SBA-15 (Cr:Mo = 0.1:0.1, 1:1, 2:2, 2/3:2, and 2:2/3, respectively). In case of introducing either chromium or molybdenum, Cr or Mo was adjusted to achieve atomic ratios of Si:Cr = 100:2 or Si:Mo = 100:2. The resultant catalysts were designated Cr-SBA-15 and Mo-SBA-15. Additionally, incipient wetness impregnation (IM) (Wang *et al.*, 2009) was also employed. For the IM, the unmodified SBA-15 (1.50 g) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were added to distilled water (20 mL) and stirred at room temperature. The amount of each element was adjusted as an atomic ratio of Si:Cr:Mo = 100:2:2. The resultant slurry was dried at 333 K for 12 h and calcined at 823 K for 5 h (heating rate = 1.8 K/min). The resultant catalyst was designated Cr,Mo-SBA-15* (Cr:Mo = 2:2).

1.2 Characterization of catalysts

The X-ray diffraction (XRD) patterns and N_2 adsorption/desorption isotherms of the catalysts were analyzed for structural properties. The XRD patterns were measured using SmartLab/R/INP/DX (Rigaku Co.) with a Cu $K\alpha$ radiation monochromator at 45 kV and 150mA. After the pretreatment at 473 K for 5 hours under vacuum, N_2 adsorption/desorption isotherms of the catalysts were measured using a BELSORPmax12 (MicrotracBEL) at 77 K, and then the specific surface areas were estimated via BET. The acidic properties of the catalysts were measured for NH_3 temperature-programed desorption using a BELCAT

(MicrotracBEL) under the following conditions. First, each catalyst was exposed to 50 sccm of He gas flow at 773 K for 1 hour as pretreatment. Second, the catalyst was treated under 50 sccm of a 5% NH_3/He gas flow for 30 min at 373 K to promote the adsorption of NH_3 as a main treatment. Finally, the catalysts were maintained under He gas at 50 sccm for 15 min and was then heated from 373 K to 883 K (heating rate = 10 K/min) under a flow of He gas at 30 sccm. The desorbed NH_3 from the catalyst was then monitored using a BELMass (MicrotracBEL) quadruple mass spectrometer, which showed a mass signal of $m/e = 16$ for NH_3 . Given that the NH_3 parent peak showed a mass signal of $m/e = 17$, however, the desorbed NH_3 is thought to have been strongly influenced by H_2O .

1.3 Evaluation of catalytic performances

The catalytic performances were measured with a fixed-bed continuous flow reactor under atmospheric pressure at 723 K. Each catalyst was pelletized and sieved to 0.85-1.70 mm. The catalysts (0.25 g) were then placed into a reactor. The catalyst pretreatment was carried out with less than 12.5 mL/min of O_2 gas flow at 723 K for 1h before the evaluations of catalytic performance. The evaluations were carried out under 15 mL/min of a reactant gas flow, which consisted of $P(\text{iso-C}_4\text{H}_{10}) = 14.4$ kPa, $P(\text{O}_2) = 12.3$ kPa and $P(\text{He}) = 74.6$ kPa, respectively as partial pressure. Homogeneous reactions were not detected under these conditions. The reaction products were detected via an on-line gas chromatograph (GC-8APT, Shimadzu Corp.) using a thermal conductivity detector (TCD) and a capillary gas chromatograph (GC-2025, Shimadzu Corp.) equipped with a flame ionization detector (FID). The columns in TCD-GC consisted of a Molecular Sieve 5A (0.2 m \times Φ 3 mm) for the detection of O_2 , CH_4 , and CO and a HayaSep R (0.2 m \times Φ 3 mm) for the detection of CO_2 , C_2 , C_3 , and C_4 species. An Rt-Almina BOND/ Na_2SO_4 (30 m \times Φ 0.53 mm) was used as a capillary column in the FID-GC to provide detailed characterizations of C_4 species.

The catalytic performances were estimated on a carbon basis. The carbon balance between the reactant and the products was within $\pm 5\%$ and other products were lower alkanes less than C_3 except for main products such as isobutene, CO and CO_2 .

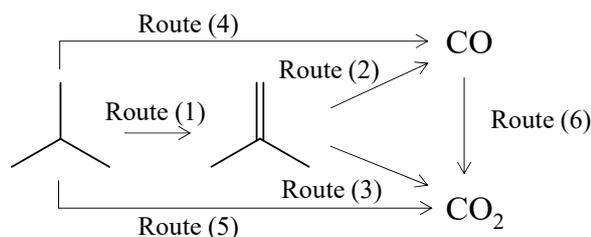
2. Results and Discussions

2.1 Catalytic performances

Figure 1 shows the catalytic performances of unmodified SBA-15 (SBA-15), Mo-SBA-15, Cr-SBA-15 and Cr,Mo-SBA-15 (Cr:Mo = 2:2). The conversion of isobutane for SBA-15 and Mo-SBA-15 were quite low, indicating that Mo did not contribute to the hydrogen abstraction from isobutane. However, the selectivity to isobutene was significantly improved from less than 40% for SBA-15 to approximately 60% for

Mo-SBA-15. Therefore, Mo did not contribute to the over-oxidation of isobutene to CO and CO₂. As expected from our previous paper on the effect that Cr exerts on the oxidative dehydrogenation of isobutane (Kato *et al.*, 2018), Cr-SBA-15 showed the highest conversion of isobutane from among the four catalysts, as shown in Figure 1. It is interesting that the binary system for Cr,Mo-SBA-15 (Cr:Mo = 2:2) showed an advantageous nature for both Mo-SBA-15 and Cr-SBA-15, which resulted in higher isobutene selectivity and stable activity during 6 h on-stream for Mo-SBA-15 and a higher conversion of isobutane for Cr-SBA-15, respectively, resulting in a higher level of isobutene yield and the suppression of a remarkable level of deactivation observed using Cr,Mo-SBA-15 (Cr:Mo = 2:2) for 6 h on-stream. It is unique when a binary catalyst reflects the advantages of the individual elements of Mo and Cr.

Figure 2 shows the catalytic performances of Cr,Mo-SBA-15 (Cr:Mo = 2:2) at several ratios of $P(O_2)$ to $P(\text{iso-C}_4\text{H}_{10})$ as reactant gas flow component. As the ratio of the partial pressure of $P(O_2)$ to $P(\text{iso-C}_4\text{H}_{10})$ was increased, the conversion of isobutane was increased, while the selectivity to isobutene was decreased, followed by an increase in the selectivities for CO and CO₂. As pointed out in our previous papers (Sugiyama *et al.*, 2015; Ehiro *et al.*, 2015, 2016a, 2016b; Kato *et al.*, 2018; Wang *et al.*, 2009), in catalysts modified with Cr alone, Cr⁶⁺ was an active site for this reaction. During oxidative dehydrogenation, Cr⁶⁺ was reduced to Cr³⁺, followed by the re-oxidation of Cr³⁺ to Cr⁶⁺ with gaseous O₂. Therefore, it is reasonable that the re-oxidation rate of Cr³⁺ was promoted with increase in the partial pressure of O₂ gas, and the total reaction rate was also increased. There are several reaction routes to CO or CO₂, as shown in Scheme 1. In this process, some of the parallel reactions of isobutane to CO or CO₂ are included because selectivities to CO and CO₂ were not close to zero even when the conversion of isobutane was quite low as with the SBA-15 or Mo-SBA-15 shown in Figure 1. However, as shown in Figure 2, the main cause of a decrease in the selectivity to isobutene seems to have been due to promotion of the consecutive reactions of isobutene to CO or CO₂ (Route (2) and (3) in Scheme 1) since the selectivities to CO and CO₂ were decreased with an increase in the conversion of isobutane.



Scheme 1 Reaction route of isobutane

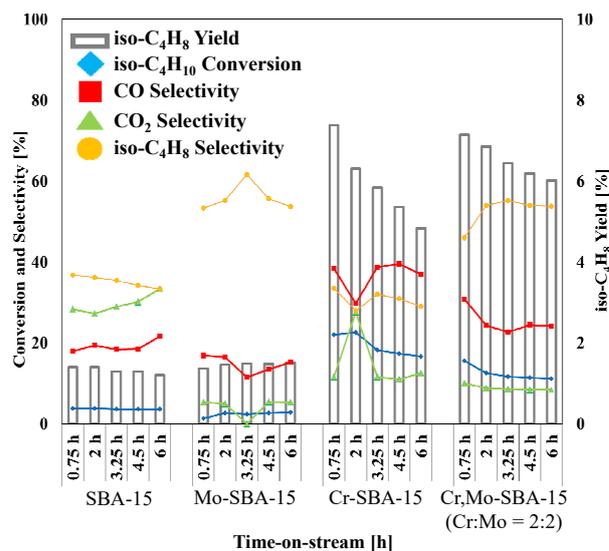


Fig. 1 Catalytic performances when using SBA-15, Mo-SBA-15, Cr-SBA-15 and Cr,Mo-SBA-15 (Cr:Mo = 2:2) for the ODH of isobutane at 723 K

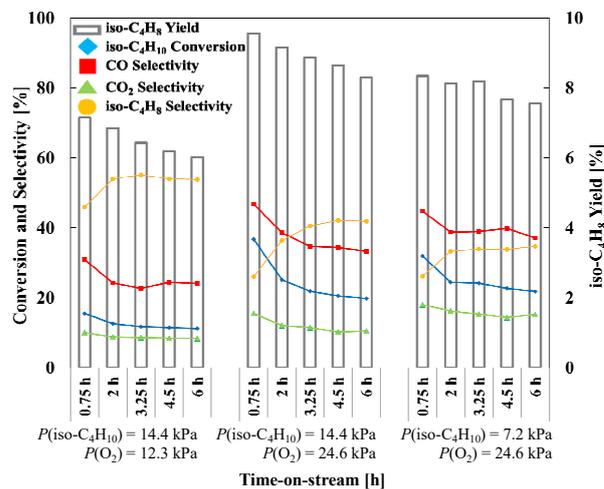


Fig. 2 Catalytic performances of Cr,Mo-SBA-15 (Cr:Mo = 2:2) for the ODH of isobutane under a reactant gas under different levels of partial pressures at 723 K

Figure 3 shows the catalytic performances of Cr,Mo-SBA-15 (Cr:Mo = 0.1:0.1, 1:1, 2:2), with differing, but equal, amounts of Cr and Mo. The conversion of isobutane was enhanced when the amounts of introducing of Cr and Mo were increased from Cr:Mo = 0.1:0.1 to Cr:Mo = 1:1. However, the conversion of isobutane did not increase at the introducing of Cr:Mo = 2:2. Additionally, isobutene selectivity remained at a higher level, regardless of the ratio. As a result, the highest yield of isobutene was detected when using Cr,Mo-SBA-15 (Cr:Mo = 1:1 and 2:2).

Figure 4 shows the catalytic performances of Cr,Mo-SBA-15 (Cr:Mo = 2:2) and Cr,Mo-SBA-15*

(Cr:Mo = 2:2), in which SBA-15 was modified with the same amounts of Cr and Mo while the preparation method differed. On Cr₂Mo-SBA-15* (Cr:Mo = 2:2), the isobutene selectivity was decreased in contrast to an increase in CO and CO₂ selectivities. Therefore, the catalyst prepared by the DM was clearly preferable for this reaction than that prepared by the IM. The reason will be discussed later. **Figure 5** shows the catalytic performances when using Cr₂Mo-SBA-15 (Cr:Mo = 2:2, 2:2/3, 2/3:2), in which the ratio of Cr to Mo was changed. The conversion of isobutane was increased when the ratio of Cr to Mo was changed from Cr:Mo = 2:2 to Cr:Mo = 2:2/3 or 2/3:2, and isobutene selectivity was decreased with increases in CO and CO₂ selectivities. As a result, the yield of isobutene was enhanced with the change in ratio.

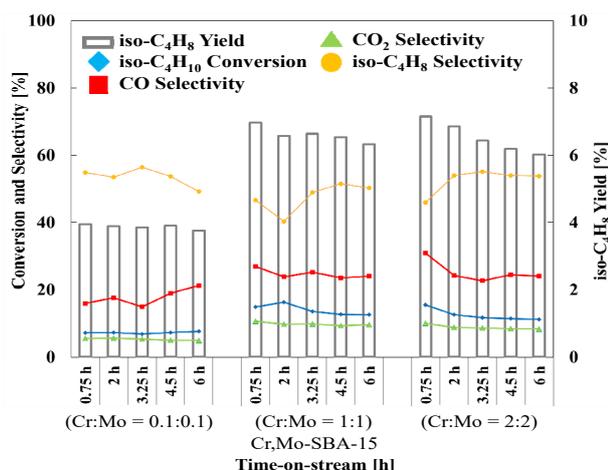


Fig. 3 Catalytic performances of Cr₂Mo-SBA-15 (Cr:Mo = 0.1:0.1, 1:1, 2:2) for the ODH of isobutane at 723 K

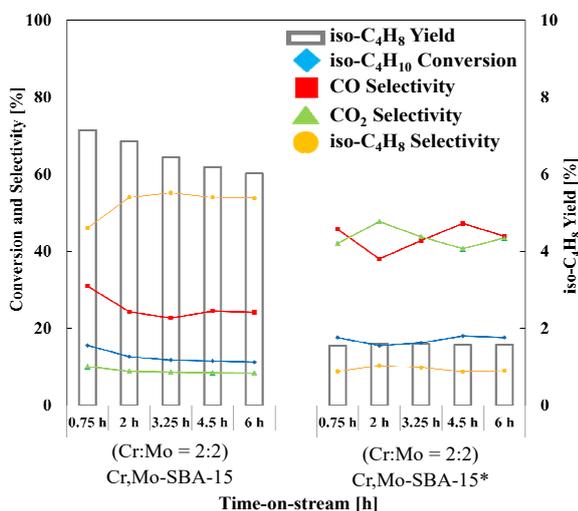


Fig. 4 Catalytic performances of Cr₂Mo-SBA-15 (Cr:Mo = 2:2) prepared via the DM method and Cr₂Mo-SBA-15* (Cr:Mo = 2:2) prepared via the IM method for the ODH of isobutane at 723 K

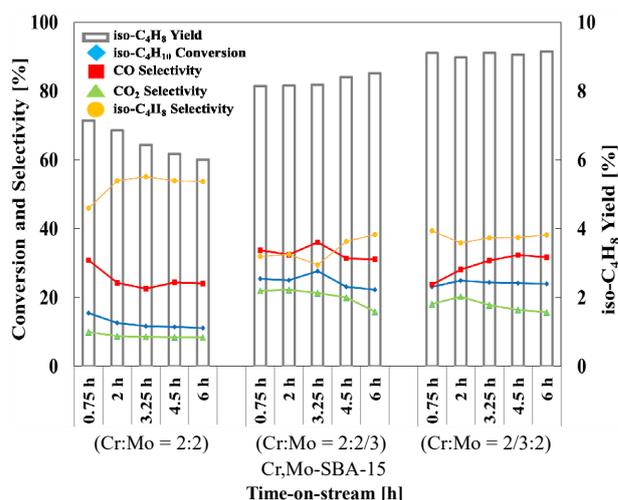


Fig. 5 Catalytic performances of Cr₂Mo-SBA-15 (Cr:Mo = 2:2, 2:2/3, 2/3:2) for the ODH of isobutane at 723 K

2.2 Characterization of Catalysts

XRD and N₂ adsorption/desorption isotherm measurements were carried out for the analysis of structural properties. The upper and lower Figures in **Figure 6** show the XRD patterns within the lower and higher diffraction angles, respectively, of SBA-15, Cr₂Mo-SBA-15 (Cr:Mo = 2:2) and Cr₂Mo-SBA-15* (Cr:Mo = 2:2). As shown by pattern (A) in the lower angle range of Figure 6, the diffractions of SBA-15 were recognized as a two-dimensional pore structure (Zhao *et al.*, 1998) due to the detection of (100), (110) and (200). The pattern (C) of Cr₂Mo-SBA-15* (Cr:Mo = 2:2) also showed peaks at the same angles. Therefore, Cr₂Mo-SBA-15* (Cr:Mo = 2:2) possessed the same pore structure as unmodified SBA-15. With also Cr-SBA-15, Mo-SBA-15 and Cr₂Mo-SBA-15 (Cr:Mo = 0.1:0.1 and 1:1), diffraction peaks due to (100), (110) and (200) were detected as with pattern (A) but shifted to an angle lower than unmodified SBA-15, which indicated an increase in d-spacing (not shown). In case of Cr₂Mo-SBA-15 (Cr:Mo = 2:2), similar pattern as other catalysts was detected but the intensity was lower. In the higher angle ranges, only the diffraction of Cr₂Mo-SBA-15* (Cr:Mo = 2:2) showed the peaks assignable to crystalline MoO₃ at $2\theta = 12.8, 23.4, 25.7, 27.4, 33.7$ and 39.1° , as reported by Hanawalt *et al.* (1938).

Figure 7 shows the N₂ adsorption/desorption isotherms of SBA-15, Cr₂Mo-SBA-15 (Cr:Mo = 2:2) and Cr₂Mo-SBA-15* (Cr:Mo = 2:2). Additionally, **Table 1** shows the specific surface areas of various catalysts, as analyzed via BET. These catalysts exhibited type IV isotherms and all isotherms had the characteristic shapes for capillary condensation into a mesopore at $p/p_0 = 0.4-0.8$ with a hysteresis loop. However, only Cr₂Mo-SBA-15 (Cr:Mo = 2:2) commenced capillary condensation at approximately $p/p_0 = 0.4-0.8$.

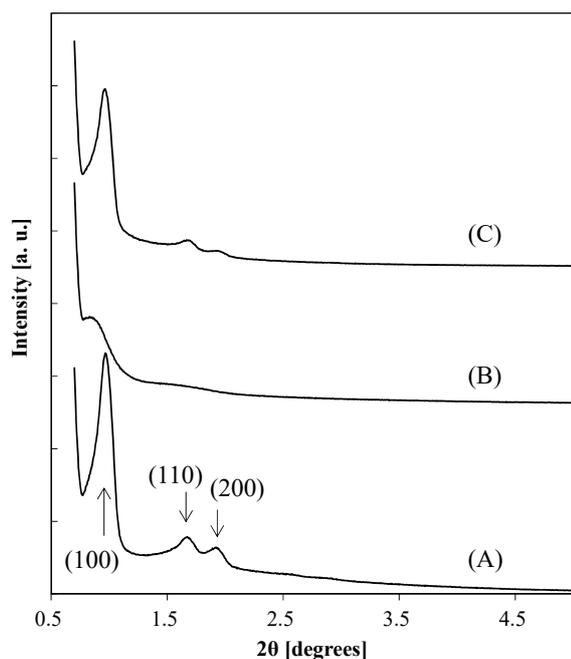


Fig. 6 XRD patterns of SBA-15 (A), Cr,Mo-SBA-15 (Cr:Mo = 2:2) (B) and Cr,Mo-SBA-15* (Cr:Mo = 2:2) (C)

The specific surface areas of the Cr,Mo-SBA-15 series were at higher levels and the greatest surface area was 872 m²/g for Cr,Mo-SBA-15 (Cr:Mo = 0.1:0.1). Cr,Mo-SBA-15* (Cr:Mo = 2:2) prepared via the IM at 270 m²/g, which was the lowest surface area of all catalysts used in the present study.

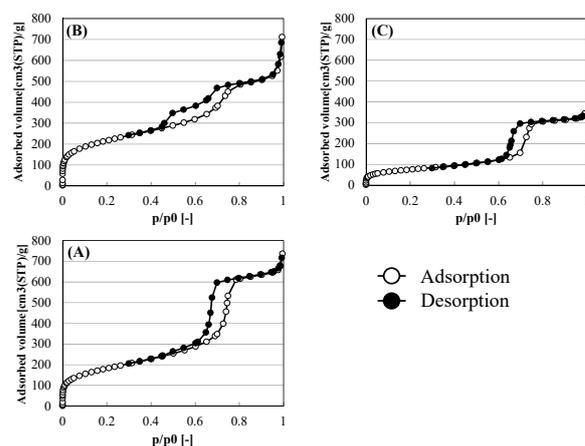


Fig. 7 N₂ adsorption-desorption isotherms of SBA-15 (A), Cr,Mo-SBA-15 (Cr:Mo = 2:2) (B) and Cr,Mo-SBA-15* (Cr:Mo = 2:2) (C)

Table 1 The specific surface area of various catalysts analyzed via BET

Catalyst	Specific surface area [m ² /g]
SBA-15	660
Cr ₂ Mo-SBA-15 (Cr:Mo = 0.1:0.1)	872
Cr ₂ Mo-SBA-15 (Cr:Mo = 1:1)	520
Cr ₂ Mo-SBA-15 (Cr:Mo = 2:2)	780
Cr-SBA-15	746
Mo-SBA-15	678
Cr ₂ Mo-SBA-15* (Cr:Mo = 2:2)	270

Figure 8 shows the NH₃-TPD of SBA-15, Mo-SBA-15, Cr-SBA-15, Cr,Mo-SBA-15 (Cr:Mo = 0.1:0.1, 1:1, 2:2) and Cr,Mo-SBA-15* (Cr:Mo = 2:2) for measuring acidic property. A peak was detected at approximately 493 K on only Cr,Mo-SBA-15* (Cr:Mo = 2:2), while no peak was detected for either SBA-15 or all SBA-15 modified with Cr and/or Mo catalysts. These results rule out the possibility that stronger acid sites promoted the parallel or consecutive reactions that contributed to decreases in isobutene selectivity (Takita *et al.*, 2005).

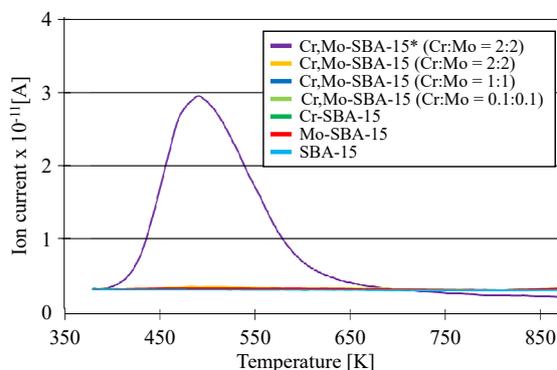
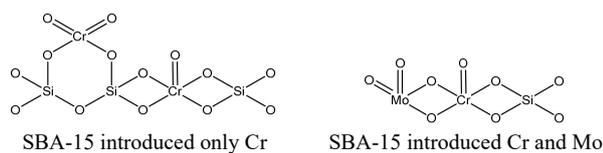


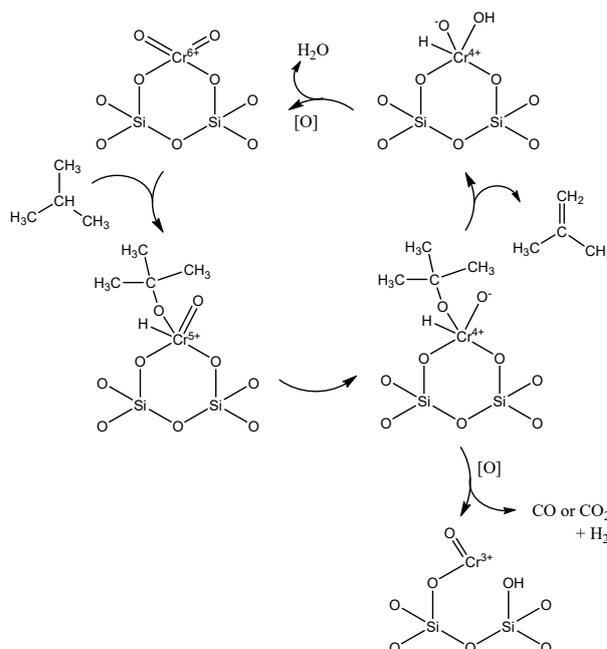
Fig. 8 NH₃-TPD of SBA-15, Mo-SBA-15, Cr-SBA-15, Cr,Mo-SBA-15 (Cr:Mo = 0.1:0.1, 1:1, 2:2) and Cr,Mo-SBA-15* (Cr:Mo = 2:2)

2.3 Reaction mechanism and the effect of introducing molybdenum

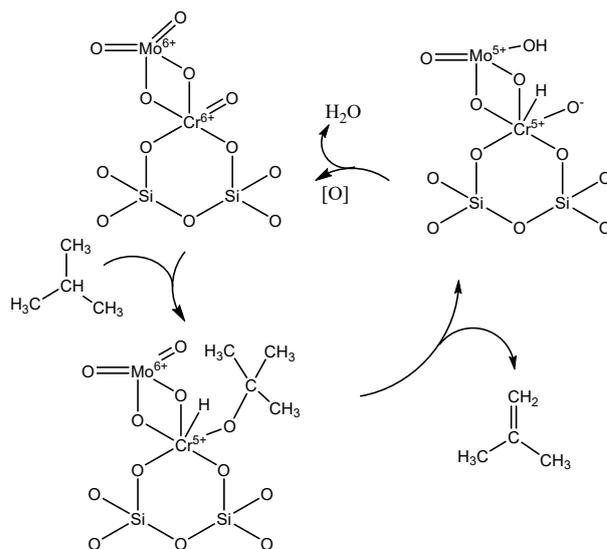
In previous papers (Sugiyama *et al.*, 2016; Kato *et al.*, 2018), we have proposed the structures of the Cr species and a reaction mechanism. **Scheme 2** (left image) shows the Cr species introduced into the silica framework of meso-porous materials and how two types of oxygen bridge Si and Cr to form a terminal double bond. Additionally, each Cr has either one or two elements of terminal oxygen. In case that Cr has two terminal oxygens, as shown **Scheme 3**, the terminal oxygen absorbs isobutane, which results in the formation of an isobutylcarbenium cation and H⁻. Then, isobutene is released from the isobutylcarbenium cation, while the remaining H⁻ and absorbed H⁺ by O⁻ formed from another terminal oxygen forms H₂O with oxygen, which is then released. However, if isobutylcarbenium cation is attacked by another terminal oxygen, consecutive reactions from isobutene to CO or CO₂ (Routes (2) and (3) in Scheme 1) seem to be promoted and isobutene selectivity is decreased. Finally, chromium species are reduced to Cr³⁺. Normally, chromium species exist as Cr⁶⁺ or Cr³⁺ because chromium species absorbing isobutylcarbenium cation and Cr⁴⁺ are transition state. Sugiyama *et al.* (2015) and Ehiro *et al.* (2016a) also reported that Cr⁶⁺ is reduced to Cr³⁺ during the reaction. In case of SBA-15 modified with molybdenum and chromium, a Cr-O-Mo bond can be formed like binary metal oxide complex as shown Scheme 2 (right image), and it is reasonable to assume that the likelihood of the existence of terminal oxygen is decreased. As a result, the possibility that terminal oxygen will attack the isobutylcarbenium cation is undoubtedly decreased as shown **Scheme 4**. Therefore, the consecutive reactions (Routes (2) and (3) in Scheme 1) are suppressed followed by an enhancement of isobutene selectivity. In this case, Mo species can take part of chromium reduction and Cr species may be more easily re-oxidized to Cr⁶⁺. This mechanism is similar to a mechanism of selective oxidation of propylene to acrolein over Bi-Mo catalyst system reported by Burrington *et al.* (1983). Additionally, Cr species don't need to be Cr³⁺. Therefore, modification with Mo helped the suppression of catalytic deactivation. As shown in Figure 5, Cr and Mo seem to have a component ratio that is the most suitable for a binary metal oxide complex.



Scheme 2 Modification of the silica framework with Cr alone (left) or with both Cr and Mo (right)



Scheme 3 Reaction mechanism of isobutane to isobutene on SBA-15 introduced only Cr



Scheme 4 Reaction mechanism of isobutane to isobutene on SBA-15 introduced Cr and Mo

Conclusions

The maximum yield of isobutene from Cr,Mo-SBA-15 (Cr:Mo = 2:2) was only slightly improved compared with SBA-15 modified with Cr alone. Cr,Mo-SBA-15 (Cr:Mo = 2:2) showed significant improvement, however, in isobutene selectivity and in the suppression of deactivation. Isobutene selectivity was increased as a result of decreases in CO and CO₂ selectivities. Therefore, Mo plays an important role in suppressing

over-oxidation to CO and CO₂. Additionally, the yield of isobutene was enhanced when the component ratio of Cr to Mo was changed from Cr:Mo = 2:2 to either Cr:Mo = 2:2/3 or 2/3:2. Although it remained unclear where the molybdenum locates, the improvement in the catalytic performance seems to have been achieved not by the particles of each metal oxide but by their proximity that is promoted by a suitable component ratio within the framework of SiO₂.

Acknowledgement

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