

Effects of Acid Treatment on the Acidic Properties and Catalytic Activity of MCM-41 for the Oxidative Dehydrogenation of Isobutane

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Abstract

Mesoporous silicas have shown promise as materials for solid catalysts or catalyst supports due to their unique characteristics. Metal-doped mesoporous silicas are known to be catalytically active in the oxidative dehydrogenation (ODH) of isobutane. However, heavy-metal-free mesoporous silicas have not been studied closely for their use as catalysts. In the present study, MCM-41 (#41 Mobil composition of matter) was acid-treated to enhance its catalytic activity, although pure MCM-41 was confirmed as catalytically inactive for the ODH of isobutane (isobutene yield = 0.9%). The pH of a slurry of as-synthesized MCM-41 was changed during acid treatment. A pH adjustment to 6.5 resulted in great improvement in catalytic activity (isobutene yield = 6.1%), but a pH adjustment to 4.5 resulted in insufficient improvement (isobutene yield = 4.5%). It was confirmed via XRD and N₂ adsorption-desorption measurement that the pH adjustment to 4.5 degraded the ordered structure of MCM-41. This degradation would be a crucial factor that would render acid treatment less effective. In addition to the acid treatment, Al doping to MCM-41 was conducted. Al doping also greatly enhanced the acidity and catalytic activity of MCM-41.

Introduction

Isobutene is a crucial chemical ingredient for butyl rubber and gasoline octane-enhancing additives (Kilicarslan, 2013). The oxidative dehydrogenation (ODH) of isobutane to isobutene is a promising reaction route since the ODH reaction has the following advantages. First, it is not governed by thermodynamic equilibrium (Al-Zahrani *et al.*, 2000). Second, it is an exothermic reaction ($\Delta H = -103$ kJ/mol) (Liebmann and Schmidt, 1999), hence, it can proceed at a lower temperature and save energy. For instance, 5 and 10% Cr/Al₂O₃ catalysts have been used to catalyze the ODH of isobutane at 523 K (Jibrila *et al.*, 2005). However, the dehydrogenation of isobutane requires a higher reaction temperature (> 783 K) (Grabowski *et al.*, 1996; Liebmann and Schmidt, 1999; Al-Zahrani *et al.*, 2000, 2001; Jibrila *et al.*, 2005; Wang *et al.*, 2009; Zhang *et al.*, 2009), because it is an endothermic reaction. Also, the naphtha-cracking process, which is a common production method for lower olefins, requires a high reaction temperature of approximately 1,093 K (Yoshiura *et al.*, 2000). Third, the reaction field of ODH is unfavorable for coke formation due to the presence of oxygen in the reactant. Without oxygen, a catalyst would likely suffer severe carbon deposition

and require the rapid regeneration of a catalyst (Liebmann and Schmidt, 1999; Al-Zahrani *et al.*, 2000, 2001; Wang *et al.*, 2009). To overcome the difficulties of the dehydrogenation of isobutane or the naphtha-cracking process, the ODH of isobutane was conducted in the present study.

Typically, various metal oxide catalysts have been investigated for use in the ODH of isobutane (Grabowski *et al.*, 1996; Al-Zahrani *et al.*, 2000, 2001; Sulikowski *et al.*, 2002; Corberán *et al.*, 2004; Jibrila *et al.*, 2005; Huerta *et al.*, 2006; Wang *et al.*, 2009; Zhang *et al.*, 2009; Wu *et al.*, 2012), because some metal oxides can show great redox properties and high conversion capabilities. However, metal oxides are potentially toxic and require additional disposal processes. Therefore, the objective of the present study was to prepare a metal-free, particularly a heavy-metal-free, and catalytically active catalyst for the ODH of isobutane.

Our research group has paid attention to mesoporous silica, MCM-41 (#41 Mobil composition of matter), as a catalyst or support. MCM-41 is a very attractive material as a heterogeneous catalyst since it has a high surface area, high thermal stability, and solid acidic properties. In fact, MCM-41 has shown great

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catalytic activity in various reaction systems such as the acetalization of cyclohexanone (Iwamoto *et al.*, 2003), aldol reactions of acetals (Ishitani and Iwamoto, 2003), and the Friedel-Crafts acylation of anisole (Ishitani *et al.*, 2008). These great catalytic activities originate from the unique acidic properties of MCM-41. In the above reaction systems, MCM-41, which has an amorphous silica wall, showed a greater catalytic activity than an amorphous silica. Moreover, it has been reported that the pore sizes of MCM-41s affected their catalytic activities in an acid-catalyzed reaction, although the investigated pore sizes were large enough for the reactant to pass through (Iwamoto *et al.*, 2003). However, reports on the use of MCM-41 as a catalyst, or as a support for a gas phase reaction, are scarce (Sulikowski *et al.*, 2002). In particular, metal-free MCM-41 has rarely been studied in the gas phase.

In our previous work, pure MCM-41 was catalytically inactive for the ODH of isobutane. Hence, the activation of MCM-41 was required in order to improve its catalytic activity. In the present study, MCM-41 was activated via simple acid treatment and aluminum doping. Furthermore, the as-synthesized aluminum-doped MCM-41 was treated with a 0.1 M NH_4F aqueous solution before calcination to improve its acidity and catalytic activity. This type of post-synthesis NH_4F treatment has mainly been used to improve Brønsted acidity without a significant change in Lewis acidity (Luque *et al.*, 2005). Hence, a post-synthesis NH_4F treatment was conducted for the as-synthesized aluminum-doped MCM-41 that was prepared in the present work to improve its acidity and catalytic activity. The catalytic activities, structural and acidic properties of the catalysts were examined in this work.

1. Experimental

1.1 Catalyst preparation

MCM-41 (referred to as M41) was prepared using a method that was developed by Iwamoto and co-workers (Iwamoto *et al.*, 2000). Dodecyltrimethylammonium bromide (33.8 g (109 mmol), Wako Pure Chemical Industries, Ltd.) dissolved in 96.2 g of distilled water and 45.9 g of colloidal silica (Snowtex 20, Nissan Chemical Ind.) was used as the surfactant template and the silica source. Sodium hydroxide (1.74 g (43.5 mmol), Wako Pure Chemical Industries, Ltd.) was dissolved in 18.8 g of distilled water and used for the pH adjustment of the solution. Colloidal silica and sodium hydroxide were alternatively added dropwise to the surfactant solution for about 20 min, and the mixed solution was stirred at 313 K for 2 h. The pH of the mixed solution was confirmed at approximately 11.5 after 2 h stirring. The hydrothermal synthesis was carried out at 413 K for 48

h without stirring. The white wet solid thus obtained was filtered, washed with distilled water, and dried at 333 K. The dried white powder was denoted as “As-synthesized M41.” Finally, M41 was obtained by calcination at 873 K for 6 h.

To improve the acidic properties and catalytic activity, the as-synthesized M41 was acid-treated with aq. HCl (Hayashi *et al.*, 2010). As-synthesized M41 was dispersed in water with a few drops of 2 M aq. HCl. Then, the pH of the solution was adjusted to 4.5, 5.5 or 6.5 by adding 2 M aq. HCl with stirring. After the pH adjustment, the solution was heated at 353 K for 20 h without stirring. The solution was then cooled, filtered, washed with distilled water, and dried at 333 K. A dried sample was calcined at 873 K for 6 h. The final products thus obtained were denoted as M41-pH4.5, M41-pH5.5, and M41-pH6.5, respectively. The preparation of M41-pH6.5 was also conducted using the templates consisting of different carbon-chain lengths, *n*-decyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and cetyltrimethylammonium bromide (all from Wako Pure Chemical Industries, Ltd.). The resultant solids were denoted as M41-C10, M41-C14, and M41-C16, respectively. The weight of the surfactant was changed to 7.98 g (21.9 mmol) when preparing M41-C16. To investigate effects of the reaction time of the hydrothermal synthesis on the catalytic activity and acidity of M41-pH6.5, 48 h of the reaction time of the hydrothermal synthesis was changed to 24 h or 72 h. Catalysts thus prepared was denoted as M41-24h or M41-72h.

For a comparison of catalytic activity, another mesoporous silica, FSM-16 (#16 Folded sheets mesoporous material) (Inagaki *et al.*, 1996), was prepared from a hydrated sodium silicate powder (Kishida Chemical Co. Ltd.; molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ = 2.00) and cetyltrimethylammonium bromide (Wako Pure Chemical Industries, Ltd.), according to a method proposed by Inagaki and co-workers (Inagaki *et al.*, 1996). In the present study, FSM-16 (referred to as F16) was also acid-treated with aq. HCl, and was denoted as F16-pH6.5.

In addition to the above acid treatment, aluminum was introduced to M41 to improve its acidic properties and catalytic activity. The introduction of aluminum was conducted via the TIE (Template Ion Exchange) method (Iwamoto and Tanaka, 2001). As-synthesized M41 (2.0 g) was dispersed in 20.0 g of distilled water, while 0.16 g (0.42 mmol) of aluminum nitrate nonahydrate was dissolved in another 20.0 g of distilled water. An aqueous solution of aluminum nitrate was added to the slurry of M41 and stirred for 1 h at room temperature. The mixed solution was heated at 353 K for 20 h. The solution was then filtered, washed with distilled water, and dried at 333 K. Finally, aluminum-

doped MCM-41 (Al-M41) was obtained by calcination at 823 K for 6 h.

As stated above, the post-synthesis NH_4F treatment has been used to enhance the acidic property of Al-MCM-41 with Si/Al ratios ranging from 40 to 15 (Luque *et al.*, 2005). Hence, the as-synthesized Al-M41 prepared by the TIE method was treated with a 0.1 M NH_4F aqueous solution by slightly modifying a procedure reported by Luque and co-workers. As-synthesized Al-M41 (2.5 g) was added to 300 mL of 0.1 M NH_4F aqueous solution and stirred for 34 h. Then, the solution was filtered, dried at room temperature, and calcined at 823 K for 24 h. The obtained sample was denoted as Al-F-M41.

For a comparison with mesoporous silicas, a fumed silica, Cab-O-Sil (Cabot Co.), was used. In addition, amorphous silica (referred to as SiO_2) was prepared using almost the same preparation procedure as that of M41-pH6.5. To obtain amorphous silica, the used amount of sodium hydroxide was reduced by one-tenth that of M41-pH6.5.

1.2 Catalyst characterization

The structural properties of the catalysts were analyzed via X-ray diffraction (XRD; RINT 2500X, Rigaku Co.) and N_2 adsorption-desorption measurement (BELSORP-18SP, Bel Japan Inc.). The powder XRD patterns of the catalysts were obtained using monochromatized $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). Before the N_2 adsorption-desorption measurement at 77 K, the catalysts were pretreated at 473 K for 10 h in a vacuum. Average pore diameter of a sample was calculated from BET surface area and total pore volume, assuming that all pores are cylinder type.

The aluminum content in the catalysts was calculated by analyzing the concentration of aluminum ion in the remaining solution obtained from the synthesis by ICP-AES (SPS3520UV, SII Nanotechnology Inc.).

The acidic properties of the catalysts were characterized via in-situ infrared spectroscopy (in-situ NH_3 -FT-IR; FTX3000MX, Bio Rad Inc., resolution of 4 cm^{-1}), temperature-programmed desorption (TPD; BELCAT-A, Bel Japan Inc.), and the use of a set of Hammett indicators.

In NH_3 -FT-IR measurement, NH_3 was used as a probe molecule for acid sites. A molded sample (10 mg) in the shape of a disc 13 mm in diameter was pretreated in a vacuum for 1 h at 723 K. A sample was then cooled to 323 K in a vacuum. First, a spectrum before the NH_3 adsorption was measured in this step. Second, the NH_3 adsorption was started by introducing 13.3 kPa of NH_3 gas to the IR cell. Desorption behavior of NH_3 was monitored at 323, 423, 523, 623, and 723 K after maintaining each temperature for 10 min.

In NH_3 -TPD measurement, a catalyst (50 mg) was loaded into a U-shaped quartz tube. Prior to each run,

the catalyst was pretreated under 50 sccm of He flow at 773 K for 1 h, and then cooled to 373 K. After this temperature was maintained for 10 min, the catalyst was treated with 50 sccm of 5% NH_3/He gas for 30 min. After the treatment, the catalyst was again kept under a He flow (50.0 sccm) for 15 min. The catalyst then was heated from 373 K to 773 K at 10 K/min flowing 30 sccm of He gas. The desorbed NH_3 from the catalyst was analyzed using a quadrupole mass spectrometer (OmniStar-s, Pfeiffer Vacuum GmbH). A fragment peak at $m/e = 16$ was used to monitor the desorbed NH_3 .

The acid strength of each catalyst was also measured using a 0.1wt% toluene solution of Hammett indicators. Methyl red ($pK_a = 4.8$; Kanto Chemical Co., Inc.), 4-phenylazo-1-naphthylamine hydrochloride ($pK_a = 4.0$; Wako Pure Chemical Industries, Ltd.), methyl yellow ($pK_a = 3.3$; Kanto Chemical Co., Inc.), 4-phenylazodiphenylamine ($pK_a = 1.5$; Kanto Chemical Co., Inc.), and dicinnamal-acetone ($pK_a = -3.0$; Tokyo Chemical Industry Co., Ltd.) were used as Hammett indicators. After each catalyst (10 mg) was added to 5 mL of a toluene solution, 0.1 mL of 0.1 wt% toluene solution of each Hammett indicator was then added to the solution, and the coloration was observed.

1.3 Catalytic activity testing

The catalytic activity tests were carried out in a fixed-bed continuous flow reactor at atmospheric pressure. Each catalyst (0.25 g) was gently pelletized in order to maintain the ordered structure, and sieved to 0.85–1.70 mm in advance. The catalyst was fixed with quartz wool and pretreated with 12.5 mL/min of O_2 gas flow at 723 K for 1 h. After the pretreatment, a catalytic activity test was started by flowing 15 mL/min of helium, isobutane and oxygen to the reactor. Their partial pressures were adjusted to $P(\text{He}) = 74.6\text{ kPa}$, $P(\text{i-C}_4\text{H}_{10}) = 14.4\text{ kPa}$, and $P(\text{O}_2) = 12.3\text{ kPa}$, respectively. Under these conditions, no homogeneous gas phase reaction was observed.

The reaction was monitored using an online gas chromatograph (GC-8APT, Shimadzu Corp.) equipped with a TCD. A molecular Sieve 5A (MS 5A, $0.2\text{ m}\times\Phi 3\text{ mm}$) for O_2 , CH_4 and CO and a Haysep R ($2.0\text{ m}\times\Phi 3\text{ mm}$) for CO_2 , C_2 , C_3 , and C_4 products were used as the columns. The carbon balance between the reactant and the products was within $\pm 5\%$. The product selectivity and isobutane conversion were calculated on a carbon basis.

2. Results and Discussion

2.1 Structural properties

The structural properties of the catalysts were studied via XRD and N_2 adsorption-desorption measurement. **Figure 1** shows the XRD patterns of M41 and F16 in a low-angle region. The peaks in a low-angle region were assigned to the (100), (110), and

Table 1 Physical properties of the catalysts

Catalyst	2θ [°]	d_{100} [Å]	a_0^a [Å]	Relative intensity of XRD (100) diffraction ^b [%]	BET surface area [m ² /g]	Total pore volume [cm ³ /g]	Average pore diameter [Å]
M41	2.66	33.19	38.32	100	788	0.61	30.7
M41-pH4.5	2.60	33.95	39.20	78.8	719	0.72	40.1
M41-pH5.5	2.60	33.95	39.20	103	743	0.64	34.4
M41-pH6.5	2.60	33.95	39.20	109	833	0.66	31.8
Al-M41	2.56	34.48	39.82	64.1	716	0.81	45.1
Al-F-M41	2.58	34.22	39.51	84.2	704	0.73	41.3
F16	2.28	38.72	44.71	183	771	0.85	44.1
F16-pH6.5	2.30	38.38	44.32	163	887	1.0	46.4
M41-C10	2.84	31.08	35.89	114	823	0.53	25.7
M41-C14	2.40	36.78	42.47	147	978	0.84	34.4
M41-C16	2.16	40.87	47.19	123	887	0.92	41.5
M41-24h	2.60	33.95	39.20	130	917	0.69	30.2
M41-72h	2.54	34.75	40.13	194	899	0.68	30.1

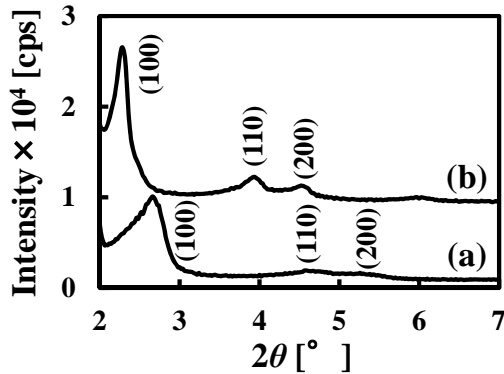
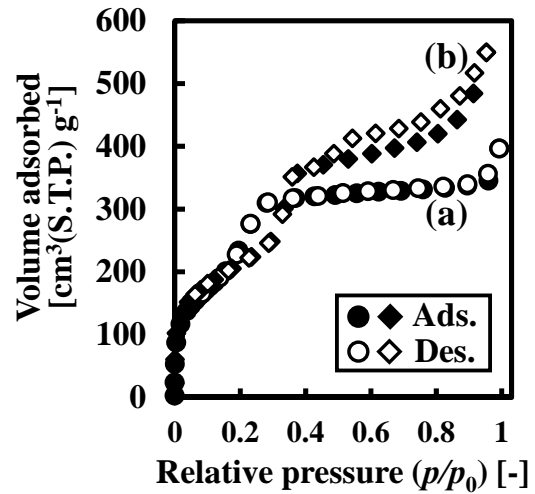
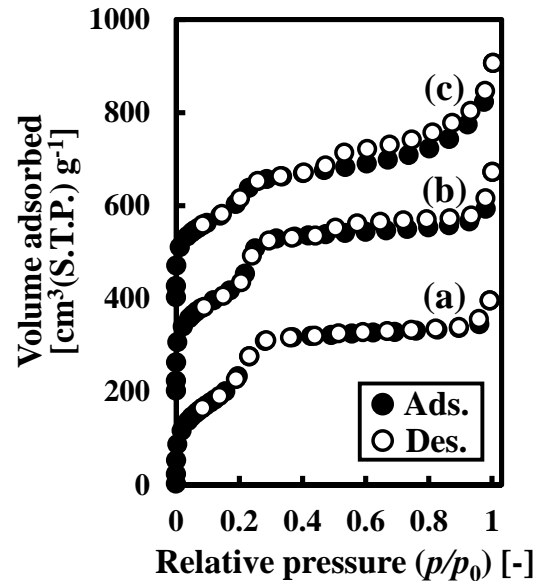
^a Lattice constant a_0 was calculated by $d_{100} \times \frac{2}{\sqrt{3}}$

^b Based on the intensity of M41

(200) planes of the hexagonally ordered structures of M41 and F16. The relative intensities of the (100) diffraction of the catalysts are summarized in **Table 1**. The peak intensities of M41-pH4.5 and Al-M41 were weakened by 15.8 and 35.9%, respectively, based on that of the parent M41. However, it was confirmed that all of the catalysts retained the hexagonally ordered structures.

Figure 2 shows the N₂ adsorption-desorption isotherms of the catalysts. Although both isotherms were categorized as type IV, their shapes were slightly different in a range of $p/p_0 > 0.3$. The isotherm of M41 had an almost plateau region in the above range of relative pressures, while that of F16 was sloping and rising. This difference can be assumed to have originated from a slightly different regularity in the hexagonal structure. The surface areas and total pore volumes of the catalysts are listed in Table 1. The catalysts that showed the weakened (100) diffractions had relatively low surface areas. As shown in **Figure 3**, the isotherm of M41-pH4.5 was slightly different from that of either M41 or M41-pH6.5 and similar to that of F16 (Figure 2). There were plateau regions for the isotherms of M41 and M41-pH6.5 after capillary condensation ($p/p_0 > 0.3$) while the adsorption isotherm of M41-pH4.5 was sloping and rising. These results suggest that the acid treatment at pH=4.5 either distorted the ordered structure of M41-pH4.5 or

partially destroyed it. In fact, the surface area of M41-pH4.5 was lower than that of M41, M41-pH5.5, or

**Fig. 1** XRD patterns of (a) M41 and (b) F16 at a low diffraction angle**Fig. 2** N₂ adsorption-desorption isotherms of (a) M41 and (b) F16**Fig. 3** N₂ adsorption-desorption isotherms of (a) M41, (b) M41-pH6.5, and (c) M41-pH4.5

M41-pH6.5 (Table 1). However, as confirmed by XRD analysis, the majority of the porous structures of the catalysts were maintained even after the acid treatment, Al doping, or NH_4F treatment, and, therefore, all surface areas were higher than $704 \text{ m}^2/\text{g}$ (Table 1).

2.2 Catalytic activity of the silica catalysts

The mesoporous silica catalysts were used for the ODH of isobutane. In addition to the mesoporous silicas, fumed silica (Cab-O-Sil, Cabot Co.) and amorphous silica were also tested. The catalytic activities of the silica catalysts are listed in **Table 2**. The catalytic activities of Cab-O-Sil and amorphous silica (SiO_2) were quite low. Moreover, it was revealed that the mesoporous silica catalysts, M41 and F16, were also catalytically inactive. However, the acid-treated M41s showed much greater catalytic capacities than that of M41. Furthermore, it was confirmed that the pH of the M41 precursor solution adjusted in the acid treatment affected the catalytic activity. A solution pH that was lower than 5.5 resulted in lower catalytic activity (Table 2). During the acid treatment, it was acceptable that an ion exchange occurred between the cationic templates and the protons from aq. HCl. Hence, the acid treatment at a lower pH was expected to promote the ion exchange and cause a partial destruction of the ordered structure because of the lack of a template. The structural destruction of M41-pH4.5 was confirmed via XRD and N_2 adsorption-desorption measurement, as mentioned above (Table 1 and Figure 3). A possible reason for the lower catalytic activity of M41-pH4.5 was the partial destruction and/or distortion of the hexagonally ordered structure that is characteristic of the parent M41. It was presumed that the regularity and/or uniformity of the pore structure could affect the intrinsic acidity of FSM-16 (Yamamoto *et al.*, 2009). Iwamoto *et al.* (2003) proposed that an assembly of weakly acidic OH on the uniform surface of MCM-41 may act as an effective and strong acid site. Considering the above reports and the present results of the characterization and catalytic activity test, the ordered mesoporous structure seemed to be essential to

great catalysis for the ODH of isobutane. The great catalytic activity of mesoporous silicas has been reported in reactions wherein the regular mesopore structures of the silica catalysts seemed to be an essential element (Ishitani and Iwamoto, 2003; Iwamoto *et al.*, 2003; Ishitani *et al.*, 2008; Yamamoto *et al.*, 2009).

Although acid treatment was very effective in improving the catalytic activity of M41, its effect was barely confirmed for F16. One of the possible reasons for the differences in the effectiveness of the acid treatment was the different pore sizes of M41 and F16. Lattice constant a_0 in Table 1 shows that the pore sizes of M41s increased as the carbon-chain lengths of the used templates increased, although a_0 would include silica wall thickness. Also, an average pore diameter of each catalyst was calculated, assuming that a completely ordered pore structure was constructed. Therefore, if a mesoporous sample was ordered insufficiently, an average pore diameter in Table 1 would tend to increase. This is because mesopores of a sample that are reflected to the calculation of average pore diameter would decrease as the ordered mesopores of a sample collapse. In fact, the average pore diameter became longer as degradation of an ordered mesostructure was caused by acid treatment (M41-pH4.5, M41-pH5.5, and M41-pH6.5 in Table 1). The pore sizes of the mesoporous silicas are considered crucially important to the catalytic activities of the acid-catalyzed reactions (Iwamoto *et al.*, 2003; Yamamoto *et al.*, 2009). To confirm the effect of the pore size on the catalytic activity, acid-treated M41s were prepared from different templates. The results obtained using XRD and N_2 adsorption-desorption measurement revealed that, by using different templates consisting of different carbon-chain lengths, mesopores with different sizes were prepared (Table 1). As shown in Table 2, no significant differences were observed in the catalytic activity between the acid-treated M41s (M41-C10, M41-pH6.5, M41-C14, and M41-C16). Hence, it was concluded that F16 and F16-pH6.5 were originally inactive for the ODH of isobutane, unlike M41 and M41-pH6.5. As discussed in the previous works (Iwamoto *et al.*, 2003; Yamamoto *et al.*, 2009), the regularities and/or uniformities of MCM-41 and FSM-16 could affect their acidities and catalytic activities in acid-catalyzed reaction. However, the numbers of acid sites which can act as active sites seemed to be different at least in the present reaction.

As previously reported, a mesoporous silica showed a greater catalytic activity due to its acidity than amorphous silica (Ishitani and Iwamoto, 2003; Iwamoto *et al.*, 2003; Ishitani *et al.*, 2008; Yamamoto *et al.*, 2009). Since the unique acidity of a mesoporous silica is produced due to its ordered structure, a well-ordered structure would be needed for a further improvement both of acidity and catalytic activity. Therefore, the ordered structure would be a key factor in the effectiveness of acid treatment, because the different

Table 2 Catalytic activities of the silica catalysts for the ODH of isobutane at 6 h on-stream

Catalyst	Conversion [%]	Selectivity [%]		Yield [%]
	i-C ₄ H ₁₀	CO _x	i-C ₄ H ₈	i-C ₄ H ₆
Cab-O-Sil	0.3	24.7	0	0
SiO ₂	4.6	56.4	15.3	0.7
M41	8.3	76.2	11.2	0.9
M41-pH4.5	11.5	53.9	39.2	4.5
M41-pH5.5	18.0	52.5	31.1	5.6
M41-pH6.5	21.7	61.1	28.2	6.1
M41-C10	18.7	49.7	33.1	6.2
M41-C14	19.0	48.0	30.3	5.8
M41-C16	20.2	58.2	28.9	5.8
M41-24h	20.1	59.3	32.1	6.5
M41-72h	19.1	61.8	30.5	5.8
F16	15.1	81.5	8.8	1.3
F16-pH6.5	15.9	73.0	9.2	1.5

catalytic activities were confirmed between M41-pH6.5 and M41-pH4.5 or F16-pH6.5. Although the ordered structures of M41 and F16 were confirmed via XRD and N₂ adsorption-desorption measurement (Figures 1 and 2), the shapes of N₂ adsorption-desorption isotherms differed slightly, as mentioned above (Figure 3). In addition, the precursors and preparation methods for F16 and M41 were different. The preparation conditions can influence a condensation degree of a silica precursor and final catalytic activity. Hence, these differences could have caused differences in the effectiveness of the acid treatment either independently or synergistically. The use of longer reaction time such as 72 h for the hydrothermal synthesis resulted in stronger intensity of XRD diffraction peaks (Table 1) and a slightly higher isobutene yield (Table 2).

In the present study, the acid-treated M41s showed greater isobutene selectivity than the other catalysts (Table 2), since active sites produced by acid treatment increased the chance of the conversion of isobutene. Comparing catalytic activity among M41-pH4.5, M41-pH5.5, and M41-pH6.5, it was confirmed that isobutene selectivity decreased as isobutane conversion increased.

2.3 The catalytic activity of Al-doped MCM-41 (Al-M41)

As summarized in Table 2, simple acid treatment improved the catalytic activity of M41. M41 doped with Al prepared via the TIE method (Al-M41) has shown greater catalytic activity than the parent MCM-41 in acid-catalyzed reactions (Murata *et al.*, 2008, 2010). Hence, aluminum was introduced to M41 via the TIE method in order to improve the acidic properties of M41. ICP-AES measurement of Al-M41 showed an

aluminum content of 1.0 wt%. The catalytic activity of Al-M41 is listed in **Table 3**. The isobutene yield was much higher by comparison with that of the parent M41, and was almost equal to that of M41-pH6.5.

Furthermore, Al-M41 was treated with a 0.1 M NH₄F aqueous solution to enhance its acidic properties. In a previous study, NH₄F post-synthesis treatment extracted aluminum that was tetrahedrally coordinated in the framework of aluminosilicate MCM-41 and changed it to octahedrally coordinated Al(O₅F) (Luque *et al.*, 2005). NH₄F treatment has also been used to increase the ratio of the number of Brønsted acid sites to that of Lewis acid sites, which produced stronger Brønsted acid sites (Luque *et al.*, 2005). The catalytic activity of the NH₄F-treated Al-M41 (Al-F-M41) is also listed in Table 3. As shown in Table 3, the catalytic activity of Al-F-M41 was slightly greater than that of Al-M41. Most aluminum ions loaded by the TIE method are known to be tetrahedrally coordinated in or on the silica wall and to lack strong Brønsted acid sites (Iwamoto *et al.*, 2001). Hence, it could be possible that the acidity of Al-M41 was enhanced by the NH₄F treatment. The NH₄F treatment mainly enhances the Brønsted acidity of Al-M41 (Luque *et al.*, 2005). However, the differences in the catalytic activity between Al-M41 and Al-F-M41 were slight. This result implies that the catalytic activity of Al-M41 mainly

Table 3 Catalytic activities of M41, Al-M41, and Al-F-M41 for the ODH of isobutane at 6 h on-stream

Catalyst	Conversion [%]	Selectivity [%]		Yield [%]
	i-C ₄ H ₁₀	CO _x	i-C ₄ H ₈	i-C ₄ H ₈
M41	8.3	76.2	11	0.9
Al-M41	20.4	66.9	27.1	5.5
Al-F-M41	20.9	64.2	29.2	6.1

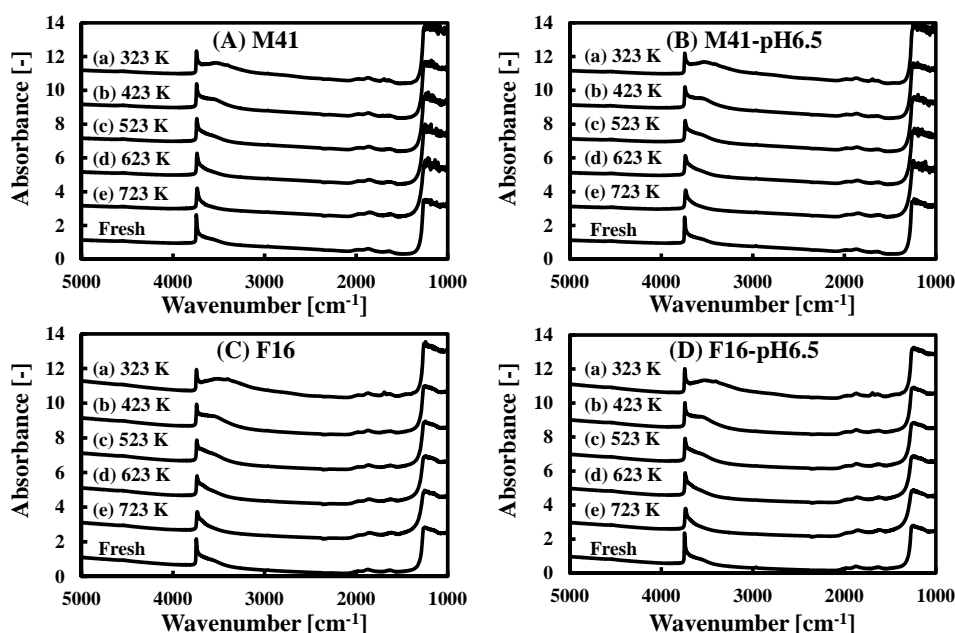


Fig. 4 NH₃-FT-IR spectra of (A) M41, (B) M41-pH6.5, (C) F16, and (D) F16-pH6.5; fresh catalysts before NH₃ adsorption at 323 K in a vacuum and NH₃ adsorbed catalysts at (a) 323 K, (b) 423 K, (c) 523 K, (d) 623 K, and (e) 723 K

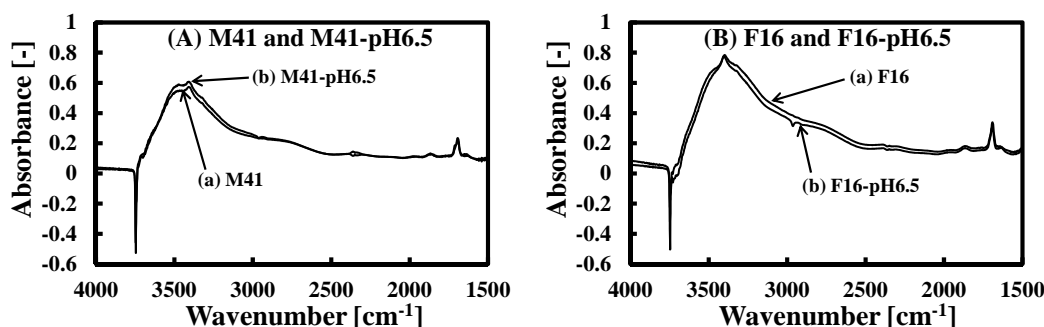


Fig. 5 Difference NH_3 -FT-IR spectra of (A) (a) M41, (b) M41-pH6.5, (B) (c) F16, and (d) F16-pH6.5 before and after NH_3 adsorption at 323 K

depends on the Lewis acidity of a catalyst. Therefore, it may be suggested that the active sites for the ODH of isobutane are Lewis acid sites and that the reaction is started by extracting the H atoms of isobutane as H^- on Lewis acid sites.

2.4 Acidic properties of the catalysts

From the NH_3 -FT-IR spectra of M41, M41-pH6.5, F16, and F16-pH6.5 (**Figure 4**), peaks were detected at $3,740\text{ cm}^{-1}$ due to the SiOH species. In the FT-IR spectra of the catalysts after NH_3 adsorption, broad peaks were evident at approximately $3,700\text{ cm}^{-1}$. These broad peaks were due to the interactions of the adsorbed NH_3 and SiOH on the surface. The intensity of these broad peaks decreased as the temperature of the IR cell increased. To confirm the acidity of the catalysts, the differences in the NH_3 -FT-IR spectra of M41, M41-pH6.5, F16, and F16-pH6.5 are shown in **Figure 5**. Each difference in the NH_3 -FT-IR spectrum was obtained from the NH_3 -FT-IR spectra before and after NH_3 adsorption at 323 K. In all catalysts, absorbance sharply dropped at approximately $3,740\text{ cm}^{-1}$ while broad peaks appeared at approximately $3,400\text{ cm}^{-1}$. This behavior indicates that isolated SiOH groups interacted with NH_3 and isolated SiOH was decreased. Although acid treatment of M41 and F16 afforded slight changes in the acidic properties (**Figure 5**), it is noteworthy that the acid treatment resulted in a great enhancement in the catalytic activity of M41, in contrast with that of F16 (**Table 2**). Since the broad peaks of either M41 or M41-pH6.5 at approximately $3,400\text{ cm}^{-1}$ were smaller than those of either F16 or F16-pH6.5, it was suggested that the acidity of both F16 and F16-pH6.5 was greater than that of both M41 and M41-pH6.5. It is worthwhile to mention that, in mesoporous silica catalysts, it has been sometimes reported that the catalytic activity did not correlate to the acidic properties estimated using FT-IR. For example, the acidic properties of FSM-16 samples with different pore sizes were evaluated by FT-IR using pyridine as a probe molecule for acid sites (Yamamoto *et al.*, 2009). Although it was expected that FSM-16 samples showed different acidic properties because of the remarkable differences in their catalytic performances in the acid-catalyzed reaction, differences in the acid amounts of

FSM-16 samples and the strength with the pore diameter were hardly distinguishable by the FT-IR characterization.

In addition to NH_3 -FT-IR, we examined NH_3 -TPD to estimate the acidities of the catalysts. **Figure 6** shows the NH_3 -TPD spectra of the Cab-O-Sil, M41, F16, acid-treated M41s, and F16-pH6.5. No desorption peak was observed for Cab-O-Sil (**Figure 6 (a)**). Two broad peaks at approximately 430 and 550 K were

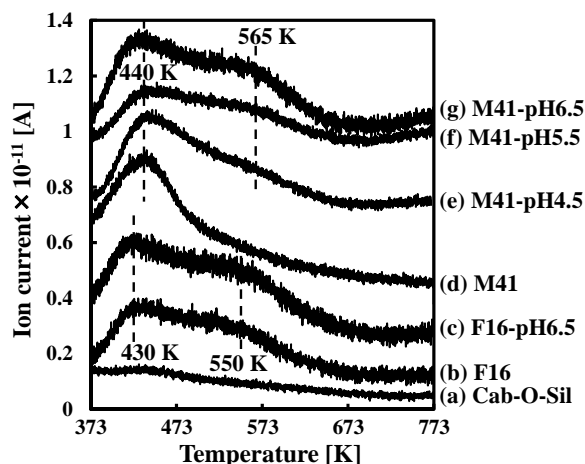


Fig. 6 NH_3 -TPD spectra of (a) Cab-O-Sil, (b) F16, (c) F16-pH6.5, (d) M41, (e) M41-pH4.5, (f) M41-pH5.5, and (g) M41-pH6.5

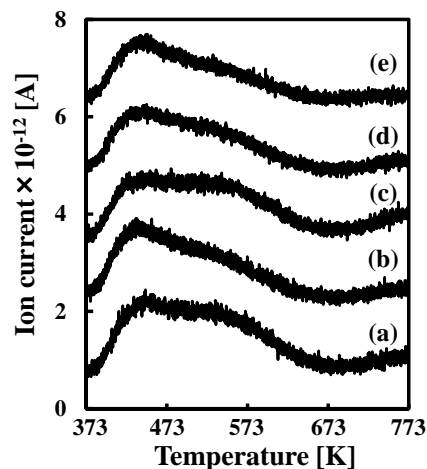


Fig. 7 NH_3 -TPD spectra of (a) M41-24h, (b) M41-72h, (c) M41-C10, (d) M41-C14, and (e) M41-C16

detected from F16, while only one peak at approximately 440 K was observed from M41 (Figures 6 (b) and (d)). Therefore, F16 seemed to have stronger acid sites than M41. This result was supported by the NH_3 -FT-IR measurement mentioned above (Figures 4 and 5). Cab-O-Sil, M41, and F16 were catalytically inactive as listed in Table 2. Hence, it was suggested that the acid sites that corresponded to the NH_3 desorption peaks under 550 K could not catalyze the ODH of isobutane. It is noteworthy that the shapes of the NH_3 -TPD spectra of acid-treated M41s were different from that of the parent M41, while only a slight difference was noted between F16 and F16-pH6.5 (Figures 6 (b)–(g)). As shown in Figures 6 (d)–(g), the peaks at approximately 565 K were the result of the acid treatment. These spectra indicate that acid treatment enhanced the acidity of M41 in contrast with that of F16. Since the improvement in the catalytic activity of M41 corresponded to the enhancement in its acidity, it can be suggested that the active sites for the ODH of isobutane are those that correspond to the desorption peaks at approximately 565 K in Figure 6. **Figure 7** shows the NH_3 -TPD spectra of the other acid-treated M41 catalysts. The shapes of their spectra are similar, but M41-24h and M41-C10 showed greater peaks in a higher temperature region than the others (Figures 7 (a) and (c)). Since the isobutene yields of both catalysts were greater than those of the others (Table 2), stronger acid sites that are produced by acid treatment would catalyze the ODH of isobutane without the aid of weaker acid sites. **Figure 8** shows the NH_3 -TPD spectra of M41, Al-M41, and Al-F-M41. The intensity of the desorption peaks was dramatically enhanced by the Al doping to M41 (Figures 8 (a) and (b)). Moreover, it was confirmed that the NH_4F treatment enhanced the acidity of Al-M41 (Figures 8 (b) and (c)). As reported previously (Luque *et al.*, 2005), adding Brønsted acid sites would enhance acidity. Although the acidity of Al-M41 was enhanced greatly, its catalytic activity was increased only slightly (Table 3). Therefore, it is conceivable that the catalytic activity depends mainly on the Lewis acidity of the catalyst.

The acid strengths of the catalysts that were evaluated in Figures 6 and 8 were also measured by Hammett indicators. M41-pH6.5, Al-M41, and Al-F-

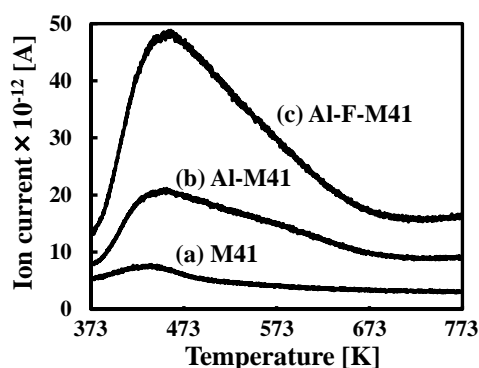


Fig. 8 NH_3 -TPD spectra of (a) M41, (b) Al-M41, and (c) Al-F-M41

M41 possessed acid sites with strengths of $pK_a = -3.0$, while the maximum acid strengths of all the other catalysts were $pK_a = 1.5$. These results further supported the NH_3 -TPD evaluation showing that acid treatment, Al doping, and NH_4F treatment enhanced the acid strength of M41 (Figures 6 and 8).

2.6 Structural properties after the ODH of isobutane

Structural properties of M41-pH6.5 were evaluated after the ODH of isobutane. **Figure 9** shows N_2 adsorption isotherms of M41-pH6.5 before and after 6 h on-stream of the ODH of isobutane at different isobutane/oxygen ratios. Since all isotherms were categorized as type IV, it was suggested that the most part of mesostructures of M41-pH6.5 remained. However, the volume adsorbed slightly decreased as the isobutane/oxygen ratio increased from 0.6 to 2.3. Physical properties calculated from N_2 adsorption-desorption measurement are listed in **Table 4**. These results revealed that greater partial pressure of oxygen in the reactant could prevent the decrease in BET surface area. In the present study, the decrease in BET surface area of M41-pH6.5 was insufficient to deactivate M41-pH6.5 because the deactivation of M41-pH6.5 could not be observed until 6 h on-stream at any isobutane/oxygen ratio. Also, XRD patterns of M41-pH6.5 before and after the reaction (**Figure 10**) showed that the diffraction pattern due to the hexagonally

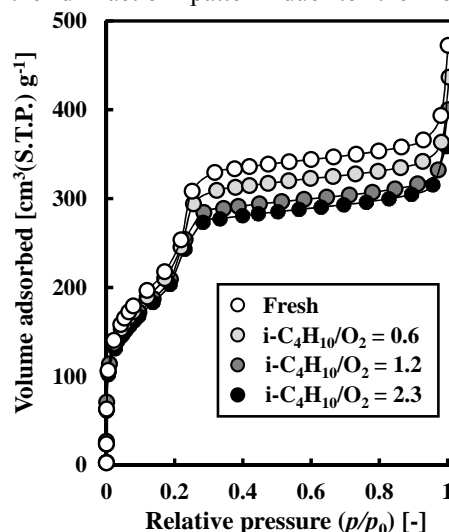


Fig. 9 N_2 adsorption isotherms of M41-pH6.5 before and after the ODH of isobutane at different isobutane/oxygen ratios and 723 K

Table 4 Physical properties of M41-pH6.5 before and after the ODH of isobutane at different isobutane/oxygen ratios and 723 K

Isobutane/oxygen [-]	BET surface area [m^2/g]	Total pore volume [cm^3/g]	Average pore diameter [\AA]
Fresh	833	0.66	31.8
0.6	804	0.60	30.6
1.2	751	0.58	30.6
2.3	738	0.54	30.1

ordered structure of M41-pH6.5 remained under the oxygen lean conditions (isobutane/oxygen = 2.3).

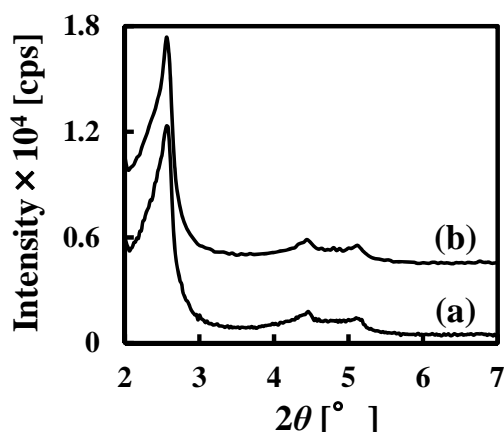


Fig. 10 XRD patterns of M41-pH6.5 (a) before and (b) after the ODH of isobutane at isobutane/oxygen = 2.3 and 723 K

Conclusions

Simple acid treatment, Al doping, and NH_4F treatment of catalytically inactive siliceous M41 resulted in a great enhancement in the catalytic activity of the ODH of isobutane on a solid catalyst. The ordered structure that is characteristic of M41 was maintained during acid treatment via a pH adjustment of between 5.5 and 6.5 to improve the catalytic activity. However, a pH adjustment to 4.5 degraded the regularity of the porous structure and led to catalytic activity that was lower than that of either M41-pH5.5 or M41-pH6.5. In contrast to M41, the advantageous effects of acid treatment were not observed for F16. Al doping of M41 was as effective as an acid treatment for improving catalytic activity. Furthermore, NH_4F treatment evidently improved the acidity of Al-M41, while its catalytic activity was only slightly improved.

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