Facile synthesis of MgO-modified mesoporous silica and its application to a CoMo-based ammonia decomposition catalyst

Takuya EHIRO¹,², Kazuaki KATAGIRI¹, Shimpei YAMAGUCHI¹ and Yayoi YOSHIOKA¹

¹Osaka Research Institute of Industrial Science and Technology, 2–7–1 Ayumino, Izumi, Osaka 594–1157, Japan

MgO-modified mesoporous silicas (MgO/SBA-15) were prepared in a one-pot synthesis method. In the present study, a silica precursor was rapidly hydrolyzed and condensed together with a Mg source under mild conditions without a hydrothermal treatment. It was confirmed that N₂ adsorption–desorption isotherms of the prepared MgO/SBA-15s were classified as type IV, which is characteristic of SBA-15. The X-ray diffraction (XRD) patterns at low diffraction angle also indicated that MgO/SBA-15s retained the ordered mesoporous structure of SBA-15, in spite of a high Mg content. On the other hand, no diffraction peaks due to Mg species were confirmed in the XRD patterns at high diffraction angle, suggesting that Mg species were dispersed on mesopores. After MgO/SBA-15s were impregnated with Co and Mo, the obtained CoMo/MgO/SBA-15 catalysts were tested for ammonia decomposition. It was revealed that the MgO content greatly influenced the catalytic activities of the CoMo-based catalysts. Although a small or large additive amount of MgO decreased the catalytic activity of CoMo/SBA-15, the modification of SBA-15 with 15 wt % of MgO resulted in the highest catalytic performance for ammonia decomposition. Moreover, the present one-pot synthesis method was more favorable for the enhancement of the catalytic activity, compared with the conventional impregnation method.

Key-words: Mesoporous silica, Basicity, One-pot synthesis, Ammonia decomposition, Hydrogen carrier

1. Introduction

Mesoporous silicas (MPSs) have received widespread interest because of their potential applications to catalysis, separation, selective adsorption, novel functional materials, and hosts to confine guest molecules due to their high surface areas combined with large and uniform pore sizes.¹ However, unmodified MPSs usually suffer from a lack of active sites necessary for adsorption or catalysis.² Therefore, it is important for a variety of applications to provide new physical and chemical properties by functionalizing the surfaces with organic or inorganic functional groups.

Controlling acidic-basic properties of MPSs is a practical way of functionalizing them. For instance, functionalization can be conducted by incorporating basic sites such as Mg species. Unlike unmodified MPSs, Mg-incorporated MPSs are applicable to catalysts,³,⁴ catalyst supports,⁵–¹⁰ adsorbents,¹¹,¹² humidity sensors,³,⁴ and drug delivery systems.¹³,¹⁴ Mg species are often introduced by impregnating Mg precursors on MPSs. However, this post-synthesis method requires two stages calcination. Therefore, a direct Mg incorporation is more desirable from the viewpoints of energy and time-efficiency. To date, one-pot synthesis methods to prepare Mg-modified SBA-15, which is a MPS with relatively large mesopores, have been reported.⁸,¹⁰,¹²,¹³,¹⁵–¹⁸ According to the previously reported papers,⁸,¹⁰,¹²,¹³,¹⁵–¹⁸ Mg-modified SBA-15s were prepared by stirring precursor solutions containing Si and Mg at 313 K for 24 h and aging them at 373 K for 24 or 48 h. In the present study, we prepared MgO-modified SBA-15 (denoted as MgO/SBA-15) more rapidly at a lower temperature to save energy and time of the preparation. Moreover, the physical and chemical properties of the obtained MgO/SBA-15s were characterized by various techniques.

Furthermore, the prepared MgO/SBA-15s were also utilized as supports for CoMo-based ammonia decomposition catalysts. Recently, ammonia has attracted much attention as a hydrogen carrier owing to its advantages such as the high energy and hydrogen density, the low flammability in air, and the moderate liquefaction conditions.¹⁹,²⁰ CoMo-based catalysts are promising alternative materials to highly catalytically active but expensive and rare Ru-based catalysts.¹⁹ Concerning ammonia decomposition catalysts, it has been reported that basicity of the catalyst supports enhanced the catalytic activities for ammonia decomposition.¹⁹,²¹ In the present study, the effects of the modifications of the catalyst support (SBA-15) with the different MgO content on the catalytic activity was investigated with the different MgO contents.
2. Experimental procedures

2.1 Materials
Tetraethoxysilane [(C₂H₅O)₄Si; TEOS, 98%], 28% aqueous ammonia (NH₃), cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O, 98%], hexaammonium heptamolybdate tetrahydrate [(NH₄)₆Mo₇O₂₄·4H₂O, 99%], magnesium acetate tetrahydrate [Mg(OAc)₂·4H₂O, 99%] were purchased from Kishida Chemical Co., Ltd. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123; PEO₆₀-PPO₇₀-PEO₆₀, average molecular weight ~5800) was purchased from Sigma-Aldrich Japan, Inc. All chemicals were used as-received without further purification.

2.2 Catalyst preparation
The flow charts shown in Fig. 1 outlines the experimental procedures to synthesize the catalyst supports. SBA-15 was prepared by referring to and modifying the previously reported method²² as follows: First, 6.0 g of P123 was dissolved in 180 g of 2 M aqueous HCl. In another vessel, 12.9 g of TEOS and 54.0 g of deionized water were mixed together. This mixed solution was added to the above 2 M aqueous HCl solution containing P123. Next, this solution was stirred vigorously at 318 K for 1 h. Then, this solution with a white precipitate was aged at 353 K for 3 h statically. After 3 h of aging, the mixture was evaporated at 353 K with stirring, dried in air, and calcined at 353 K for 3 h. The aged SBA-15 was prepared in the same procedure while a reference sample, SBA-15-IM, was prepared by calcining Mg(OAc)₂·4H₂O at 823 K for 3 h as a reference sample.

Fig. 1. The flow charts of the catalyst support preparations.

2.3 Characterization
N₂ adsorption–desorption measurements were conducted at 77 K (BELSORP-maxII, MicrotracBEL Corp.). Prior to the measurements, the catalysts were evacuated at 573 K for 3 h. The Brunauer–Emmett–Teller (BET) surface area and the pore size distribution were obtained by analyzing the N₂ adsorption isotherm via the BET²³ and the Barrett, Joyner, and Halenda (BJH) method,²⁴ respectively. The morphologies and elemental maps of the samples were confirmed by scanning electron microscope (SEM; Regulus 8230, Hitachi High-Technologies Corp.) equipped with an energy dispersive X-ray (EDX) detector. X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (SmartLab, Rigaku Corp.) using monochromatized Cu Kα radiation (λ = 0.15418 nm). A Fourier-transformed infrared attenuated total reflectance (FT-IR ATR) spectra were collected by using a Vertex 70 (Bruker Corp.). Thermogravimetric (TG) analyses were performed on a STA7300 (Hitachi High-Technologies Corp.) under 200 mL/min of air flow with a heating rate of 10 K/min from 313 to 1123 K. Basic properties of xMgO/SBA-15 were estimated by dispersing 0.5 g of each sample to distilled water and monitoring the pH values of the slurries. Each equilibrium pH value was compared as a measurement of solid basicity. Chemical state of Mo and Co were estimated via an X-ray photoelectron spectroscopy (XPS) equipped with monochromatized Al Kα radiation source (PHI Quantera II, Ulvac-PHI, Inc.). The binding energies were calibrated with respect to signal for C 1s at 284.8 eV.

2.4 Catalytic activity testing
The catalytic activity of each catalyst was tested in a fixed bed continuous flow reactor at atmospheric pressure. Each catalyst (0.2 g) was pelleted and sieved to 0.85–1.70 mm. They were fixed with quartz wool and pretreated with 40 mL/min of NH₃ gas flow at 973 K for 1 h to nitride cobalt and molybdenum oxide of the fresh catalysts and form Co₃Mo₅Nₓ, which is highly catalytically active. After the pretreatment, the catalytic activity test at 773 K was started by streaming 40 mL/min of NH₃ gas. After the unreacted NH₃ gas was trapped with a sulfuric acid
solution, the total flow rate of the produced gases was measured. Two moles of ammonia can be decomposed to 1 mol of nitrogen and 3 mols of hydrogen (2NH₃ → N₂ + 3H₂). Therefore, the hydrogen formation rate was calculated from the flow rates of inlet and outlet gases, assuming that the produced gas was composed of nitrogen and hydrogen.

3. Results and discussion

3.1 Physical properties of MgO-modified MPSs

As shown in Fig. 2(a), the isotherms of SBA-15 and MgO-modified SBA-15 were classified as type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification.²⁵) Also, all the isotherms showed the H1 type hysteresis loops, which are characteristics of cylindrical mesopores. The capillary condensation around the relative pressure of p/p₀ = 0.7 indicated the formation of mesopores with uniform sizes. By modifying SBA-15 with 1 wt% of MgO, its total pore volume increased while the further addition of MgO decreased them. Figure 2(b) shows the pore size distributions obtained by analyzing the isotherms. The pore size distribution of SBA-15 showed the sharp peak at 7.3 nm, indicating the formation of the ordered mesostructure. The peak position shifted from 7.3 to 8.5 nm by adding the small amount of Mg(OAc)₂·4H₂O [Fig. 2(b) and Table 1]. As reported previously,²⁶) Mg²⁺ ions are known as salting-in ions, water-structure-breakers, or chaotropic ions, while AcO⁻ ions dehydrate the PEO moieties of the P123 and develop hydrophilic PPO moieties due to its salting-out nature. Therefore, AcO⁻ ions possess the opposite characteristics and can change the phobicity of its PPO moieties. On the contrary, Mg²⁺ ions with the salting-in nature has the opposite effects to AcO⁻ ions and can increase surface area and total pore volume.²⁶)

Since AcO⁻ ions can develop the hydrophobic PPO moieties and reduce the hydrophilic PEO moieties in which the condensation of TEOS takes place, the above enlargement of mesopores would have been caused by AcO⁻ ions with salting-out nature. Simultaneously, Mg²⁺ ions with the salting-in nature may have contributed to increasing the BET surface area and the total pore volume of SBA-15. Although it was difficult to discuss the mechanism of change in porosity due to the opposite natures of Mg²⁺ and AcO⁻ ions and their impregnation, both the above ions may have affected the mesoporous structures of MgO/SBA-15s under the present preparation conditions. Moreover, 15MgO/SBA-15 showed the higher BET surface area than 15MgO/SBA-15-IM. This may have been due to the salting-in nature of Mg²⁺ ions and the absence of the blockage of mesopores with MgO. Therefore, it was revealed that the present one-pot synthesis is favorable to keep a high porosity. Although the porosity of SBA-15 decreased as the amount of MgO increased, all the samples possessed the mesopores and the high surface areas.

Figure 3 shows the XRD patterns of SBA-15 and MgO-modified SBA-15s. The peaks at low diffraction angle indicate the formation of the hexagonally ordered structure of MPSs. Lattice constants (a₀) was calculated as type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification.²⁵) Also, all the isotherms showed the H1 type hysteresis loops, which are characteristics of cylindrical mesopores. The capillary condensation around the relative pressure of p/p₀ = 0.7 indicated the formation of mesopores with uniform sizes. By modifying SBA-15 with 1 wt% of MgO, its total pore volume increased while the further addition of MgO decreased them. Figure 2(b) shows the pore size distributions obtained by analyzing the isotherms. The pore size distribution of SBA-15 showed the sharp peak at 7.3 nm, indicating the formation of the ordered mesostructure. The peak position shifted from 7.3 to 8.5 nm by adding the small amount of Mg(OAc)₂·4H₂O [Fig. 2(b) and Table 1]. As reported previously,²⁶) Mg²⁺ ions are known as salting-in ions, water-structure-breakers, or chaotropic ions, while AcO⁻ ions dehydrate the PEO moieties of the P123 and develop hydrophilic PPO moieties due to its salting-out nature. Therefore, AcO⁻ ions possess the opposite characteristics and can change the phobicity of its PPO moieties. On the contrary, Mg²⁺ ions with the salting-in nature has the opposite effects to AcO⁻ ions and can increase surface area and total pore volume.²⁶)

Since AcO⁻ ions can develop the hydrophobic PPO moieties and reduce the hydrophilic PEO moieties in which the condensation of TEOS takes place, the above enlargement of mesopores would have been caused by AcO⁻ ions with salting-out nature. Simultaneously, Mg²⁺ ions with the salting-in nature may have contributed to increasing the BET surface area and the total pore volume of SBA-15. Although it was difficult to discuss the mechanism of change in porosity due to the opposite natures of Mg²⁺ and AcO⁻ ions and their impregnation, both the above ions may have affected the mesoporous structures of MgO/SBA-15s under the present preparation conditions. Moreover, 15MgO/SBA-15 showed the higher BET surface area than 15MgO/SBA-15-IM. This may have been due to the salting-in nature of Mg²⁺ ions and the absence of the blockage of mesopores with MgO. Therefore, it was revealed that the present one-pot synthesis is favorable to keep a high porosity. Although the porosity of SBA-15 decreased as the amount of MgO increased, all the samples possessed the mesopores and the high surface areas.

Figure 3 shows the XRD patterns of SBA-15 and MgO-modified SBA-15s. The peaks at low diffraction angle indicate the formation of the hexagonally ordered structure of MPSs. Lattice constants (a₀) was calculated as type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification.²⁵) Also, all the isotherms showed the H1 type hysteresis loops, which are characteristics of cylindrical mesopores. The capillary condensation around the relative pressure of p/p₀ = 0.7 indicated the formation of mesopores with uniform sizes. By modifying SBA-15 with 1 wt% of MgO, its total pore volume increased while the further addition of MgO decreased them. Figure 2(b) shows the pore size distributions obtained by analyzing the isotherms. The pore size distribution of SBA-15 showed the sharp peak at 7.3 nm, indicating the formation of the ordered mesostructure. The peak position shifted from 7.3 to 8.5 nm by adding the small amount of Mg(OAc)₂·4H₂O [Fig. 2(b) and Table 1]. As reported previously,²⁶) Mg²⁺ ions are known as salting-in ions, water-structure-breakers, or chaotropic ions, while AcO⁻ ions are known as salting-out ions, water-structure-makers, or kosmotropic ions. Therefore, the above ions possess the opposite characteristics and can change the P123 micellar environment. AcO⁻ ions favor the formation of the non-polar environment for the P123 and develop hydrophobicity of its PPO moieties. On the contrary, Mg²⁺ ions with the salting-in nature has the opposite effects to AcO⁻ ions and can increase surface area and total pore volume.²⁶)

Since AcO⁻ ions can develop the hydrophobic PPO moieties and reduce the hydrophilic PEO moieties in which the condensation of TEOS takes place, the above enlargement of mesopores would have been caused by AcO⁻ ions with salting-out nature. Simultaneously, Mg²⁺ ions with the salting-in nature may have contributed to increasing the BET surface area and the total pore volume of SBA-15. Although it was difficult to discuss the mechanism of change in porosity due to the opposite natures of Mg²⁺ and AcO⁻ ions and their impregnation, both the above ions may have affected the mesoporous structures of MgO/SBA-15s under the present preparation conditions. Moreover, 15MgO/SBA-15 showed the higher BET surface area than 15MgO/SBA-15-IM. This may have been due to the salting-in nature of Mg²⁺ ions and the absence of the blockage of mesopores with MgO. Therefore, it was revealed that the present one-pot synthesis is favorable to keep a high porosity. Although the porosity of SBA-15 decreased as the amount of MgO increased, all the samples possessed the mesopores and the high surface areas.

*Fig. 2.* (a) N₂ adsorption–desorption isotherms and (b) BJH pore size distributions of SBA-15, 1MgO/SBA-15, 5MgO/SBA-15, 15MgO/SBA-15, 30MgO/SBA-15, and 15MgO/SBA-15-IM.

| Sample     | S_BET² | V_total² | a₀² | d_HM² | Wall thickness² |
|------------|--------|---------|-----|-------|----------------|
| SBA-15     | 459    | 0.78    | 10.3| 7.3   | 2.9            |
| 1MgO/SBA-15| 519    | 0.96    | 10.5| 8.5   | 2.1            |
| 5MgO/SBA-15| 407    | 0.76    | 10.8| 7.3   | 3.5            |
| 15MgO/SBA-15| 343    | 0.61    | 11.1| 7.3   | 3.8            |
| 30MgO/SBA-15| 259    | 0.48    | 10.9| 7.3   | 3.6            |
| 15MgO/SBA-15-IM | 296 | 0.57    | 10.8| 7.1   | 3.7            |

²Specific surface area calculated by BET method.
²Total pore volume obtained at the relative pressure of p/p₀ = 0.99.
²Lattice constant calculated by a₀ = 2·3¹/₂·d_HM.
²Mesopore diameter calculated by BJH method.
²Wall thickness calculated from a₀ and d_HM.
from the d-spacing values of the first peak at ca. 0.9° (d_{100}) (Table 1). These lattice constants correspond to the distance between a center of a hexagonally ordered mesopore and its neighboring center. Therefore, the wall thickness was estimated from d_0 and the pore size (d_{BET}). As summarized in Table 1, the wall thickness of 1MgO/SBA-15 was thinner than that of SBA-15. As mentioned above, the hydrophobic PPO moieties could be developed due to the salting-out effects of AcO⁻ ions, while the hydrophilic PEO moieties in which the condensation of TEOS takes place could be thinner. The enlargement of mesopores due to salting-out effects were also reported in the preparation of SBA-15 with salting-out NaCl.²²) Also, the wall thickness increased as the additive amount of Mg(OAc)₂ increased. These results implied that MgO was coated on the silica walls of SBA-15. In comparison of the synthesis methods, 15MgO/SBA-15 possessed the thinner wall than 15MgO/SBA-15-IM. Additionally, the peak intensity of SBA-15 at ca. 0.9° intensified by adding Mg(OAc)₂ to the precursor solution [Fig. 3(A)]. As discussed previously,²⁶) the increase in the peak intensity may have resulted from the formation of the smooth MgO layer on the silica walls. On the other hand, no peaks due to Mg species were detected for MgO/SBA-15 samples even up to 30 wt % of MgO while MgO crystals were formed by calcining Mg(OAc)₂ [Fig. 3(B)]. When SBA-15 was impregnated with 30 wt % of MgO, the XRD peaks due to MgO were relatively strong (not shown), while the peaks were not detected for 30MgO/SBA-15. Hence, the XRD patterns at high diffraction angle suggested that Mg species were dispersed on silica walls by the present one-pot synthesis method.

The morphologies of SBA-15 and 15MgO/SBA-15 were observed by using a SEM (Fig. 4). Both the particles were fibrous and similar in shape. In addition, the particles were composed of rod-like units which are characteristic of SBA-15. Also, there were many fragmental and small particles for both the samples. In the present study, it is expected that a shear flow with a relatively high viscosity occurred in a beaker during the evaporation. In this step, it was considerable that fibrous particles of SBA-15 and MgO/SBA-15s were somewhat broken into smaller particles, and their porosities were partially degraded. Furthermore, 15MgO/SBA-15 was analyzed by an EDX detector [Fig. 4(c)]. It was revealed that Mg species were homogeneously disperse in the particle. Moreover, no isolated SBA-15 (SiO₂) or MgO particles were confirmed by observing 500 particles of 15MgO/SBA-15. Therefore, it was presumed that MgO was homogeneously introduced to SBA-15.

3.2 Chemical properties of Mg-modified MPSs

The FT-IR spectra were recorded for MgO, SBA-15, MgO/SBA-15s, and MgO/SBA-15-IM by the ATR method (Fig. 5). The absorption bands of SBA-15 around 452, 801, and 1070 cm⁻¹ would be ascribed to Si–O–Si stretching vibration, while the absorption band around 968 cm⁻¹ would belong to Si–OH bending vibration.²⁷) For SBA-15 and MgO/SBA-15s, the peak around 1070 cm⁻¹ shifted toward a lower wavenumber side as the MgO content increased. These peak shifts were due to the interactions between Si and Mg species.¹⁰) The shift amount of 15MgO/SBA-15 was greater than that of 15MgO/SBA-15-IM. Therefore, it was suggested that the greater amount of Mg species was incorporated into the silica walls in the one-pot synthesis method. Furthermore, the peak centered at ca. 370 cm⁻¹ was confirmed for MgO. In this far-infrared region, the peak of SBA-15 became broader by adding the greater amount of Mg(OAc)₂ to the precursor solution. Hence, these behaviors of the FT-IR spectra suggested that MgO was formed on SBA-15.

To investigate the states of Mg species, the TG curves of as-synthesized SBA-15 and as-synthesized 15MgO/SBA-15 were obtained (Fig. 6). As shown in Fig. 6(a), the TG curve of as-synthesized SBA-15 dropped sharply. This peak corresponded to the peak at ca. 450 K in the derivative thermogravimetric (DTG) curve of SBA-15 [Fig. 6(b)]. According to the previously reported paper,²⁸) this weight loss is due to the P123 inside the silica walls. The following
weight loss corresponded to the small peak in the DTG curve at ca. 500 K. This weight loss was considered to be ascribed to the decomposition of P123 which was impregnated on the external surfaces of SBA-15 since the pure P123 decomposed at about 483 K. Hence, it was confirmed that the silica walls catalyzed the decomposition of P123, as mentioned previously. By adding Mg(OAc)$_2$·4H$_2$O to the precursor, the decomposition temperature of the P123 shifted toward a higher temperature. As shown in Fig. 6(b), the DTG curve showed the main peak and the shoulder peak at ca. 573 K and ca. 673 K, respectively. These TG behaviors at a high temperature region suggested the strong interaction between Mg$^{2+}$ and O atoms of the PEO moieties of the P123. According to the previously reported papers, Mg$^{2+}$ ions of as-synthesized 15MgO/SBA-15 were considered to interact strongly with O atoms of the PEO moieties of the P123, creating helical crown-ether-like Mg$^{2+}$-PEO complexes. Also, it was considered that the high mobility of the P123 would have enabled Mg$^{2+}$ ions to enter mesopores occluded with the P123.
during the evaporation step. Therefore, the above interaction would be one of key factors to the high dispersiveness of MgO on SBA-15 which was suggested by the XRD measurements [Fig. 3(B)]. To evaluate their numbers of basic sites, the equilibrium pH values of the slurries of SBA-15 and MgO/SBA-15s were noted (Table 2). No significant pH change was confirmed for SBA-15. This result indicated the insufficient acidic-basic properties of SBA-15 for this measurement. On the contrary, the pH value increased as the MgO content increased. Although CO2 dissolved in distilled water and adsorbed on MgO/SBA-15s may have affected the equilibrium pH values to some extent, these results showed that the number of the basic sites on SBA-15 was increased by the modification with the greater number of MgO. Hence, it was revealed that SBA-15 was provided with solid basicity through the present one-pot synthesis method. Compared with 15MgO/SBA-15-IM, the equilibrium pH value of 15MgO/SBA-15 was lower. This result may have been related to the interactions between Si and Mg species which were suggested from the FT-IR spectra (Fig. 5).

### Application of Mg-modified MPSs to catalyst supports for ammonia decomposition

The prepared MgO/SBA-15s were utilized as catalyst supports for ammonia decomposition. Figure 7 shows the hydrogen formation rates through ammonia decomposition at 773 K on the CoMo-based catalysts with different MgO contents. As shown in Fig. 7, it was revealed that the MgO contents of the catalyst supports significantly influenced their catalytic activities. Although 1MgO/SBA-15 showed the highest BET surface area (Table 1), the addition of 1 wt% of MgO significantly decreased the original catalytic activity of CoMo/SBA-15. On the other hand, the hydrogen formation rate increased as the MgO content increased from 1 to 15 wt%. This increasing tendency was probably due to the enhancement of its basicity (Table 2) since the promoting effects of solid basicity have been reported for ammonia decomposition catalysts.\(^{[19,21]}\) Therefore, the hydrogen formation rates of CoMo/10MgO/SBA-15 and CoMo/15MgO/SBA-15 exceeded that of CoMo/SBA-15. However, the hydrogen formation rate dropped from 15 to 30 wt% of MgO content. Consequently, the volcano-like shape was confirmed among the investigated MgO contents. Moreover, it is worth noting that the hydrogen formation rate of CoMo/15MgO/SBA-15 (185 molH₂/molmetal·h⁻¹) was higher than that of CoMo/15MgO/SBA-15-IM (168 molH₂/molmetal·h⁻¹). Since the number of basic sites of 15MgO/SBA-15 was higher than that of 15MgO/SBA-15 (Table 2), the higher hydrogen formation rate may have been owing to the higher BET surface area (Table 1). Therefore, it was revealed that the present one-pot synthesis method is a more effective method than the conventional impregnation method to prepare a basic MgO-containing support for ammonia decomposition.

### XRD patterns of the used catalysts

Figure 8 shows the XRD patterns of the used catalysts; (a) CoMo/SBA-15, (b) CoMo/1MgO/SBA-15, (c) CoMo/5MgO/SBA-15, (d) CoMo/15MgO/SBA-15, (e) CoMo/30MgO/SBA-15, and (f) CoMo/15MgO/SBA-15-IM. The observed peaks could be indexed to Co₃Mo₃N (PDF#01-089-7953), which is a highly catalytically active phase for ammonia decomposition. These results indicate that Co and Mo species were nitrided during the pretreatment under ammonia flow at 973 K. Among the present catalysts, the used CoMo/1MgO/SBA-15 indicated the strongest diffraction intensity due to Co₃Mo₃N. Generally, small particle size is desired for a high catalytic activity. Hence, the significant decrease in hydrogen formation rate would be mainly ascribed to the larger Co₃Mo₃N crystal size of CoMo/1MgO/SBA-15. As shown in Table 2, MgO/SBA-15s possessed basic sites. Therefore, the depositions of Co and Mo species may have

### Table 2. Equilibrium pH values of the slurries of SBA-15, xMgO/SBA-15 (x = 1, 5, 15, and 30), and 15MgO/SBA-15-IM

| Equilibrium pH | 1MgO/SBA-15 | 5MgO/SBA-15 | 15MgO/SBA-15 | 30MgO/SBA-15 | 15MgO/SBA-15-IM |
|----------------|-------------|-------------|--------------|--------------|-----------------|
|                | 8.5         | 9.4         | 9.7          | 10.3         | 9.9             |

*No significant pH change was observed.*

---

**Figure 7** Hydrogen formation rates of the CoMo-based catalysts with the different MgO contents.

**Figure 8** XRD patterns of the used catalysts; (a) CoMo/SBA-15, (b) CoMo/1MgO/SBA-15, (c) CoMo/5MgO/SBA-15, (d) CoMo/15MgO/SBA-15, (e) CoMo/30MgO/SBA-15, and (f) CoMo/15MgO/SBA-15-IM.
been induced especially near basic sites of MgO/SBA-15 during the impregnation step. It was considerable that relatively large particles were deposited on 1MgO/SBA-15 due to its smallest number of basic sites while Co and Mo particles could be more dispersed as the number of basic sites increased.

Figure 9 shows the XPS spectra of the used catalysts. The XPS spectra of Co 2p3/2 showed the peaks at 782 and 787 eV which represent the existence of Co2+ and Co3+, of which Co3Mo3N is mainly composed.30 The peak positions shifted when impregnating SBA-15 with MgO which is greater or equal to 5 wt%. The peak shifts implied interactions between MgO-modified surfaces and active species. Similar peak shifts were also confirmed in the XPS spectra of Mo 3d. These interactions may have prevented the formation of large Co3Mo3N particles on Co/MgO/SBA-15, CoMo/5MgO/SBA-15, CoMo/15MgO/SBA-15, CoMo/30MgO/SBA-15, and CoMo/15MgO/SBA-15-IM (Fig. 8). Moreover, according to the previous reports,30,31 the peaks located at 228.3 and 232.4 eV corresponded to Mo2+/Mo3+ (2 < δ < 4) and Mo6+ in Mo 3d5/2, respectively. The main peaks of our catalysts were positioned at around 232 eV. Hence, this result indicated higher oxidation states of Mo species such as Mo6+, of which Co3Mo3N is mainly composed. In addition to the main peaks, the weak peaks at around 228 eV was observed. Among the used catalysts, the relatively strong peak was confirmed for CoMo/1MgO/SBA-15 at around 228 eV. According to the previous study,30 it was suggested that the relatively greater amount of γ-Mo2N formed on CoMo/1MgO/SBA-15. The greater formation of γ-Mo2N leads to the insufficient formation of Co3Mo3N species, which is highly active species. Therefore, in addition to the large Co3Mo3N particle size, these different chemical states of active species may have also decreased the catalytic activity of CoMo/1MgO/SBA-15.

On the other hand, it was considered that the decrease in hydrogen formation rate from 15 to 30 wt% of MgO was partially due to its lower BET surface area (Table 1). However, similar volcano-like shape was seen in the hydrogen formation rates divided by the BET surface area of the corresponding catalyst supports (Fig. 7). These results implied that there was another inhibiting factor as well as the BET surface area. Considering the strong affinity between MgO and Mo species,6 it was presumed that a part of Mo species may have been incorporated into the MgO layer. The above incorporation of Mo species could reduce the number of active sites and hinder the synergistic effects between Co and Mo. It has been reported that CoMo bimetallic catalytic systems are more active than monometallic Co or Mo catalytic systems.9,12 Hence, the incorporation of Mo species may have been another inhibiting factor.

From these results, it was concluded that 15 wt% of MgO content of MgO/SBA-15 was the most suitable for its application to a catalyst support for ammonia decomposition while a too small or too large amount of MgO was inhibiting.

4. Conclusions

MgO-modified SBA-15s were prepared in the one-pot synthesis method without a hydrothermal treatment. It was confirmed via N2 adsorption–desorption and XRD measurements that the ordered mesostructure remained even after the modification of SBA-15 with up to 30 wt% of MgO. In addition, any diffraction peaks due to Mg species could not be detected in the XRD patterns. The elemental mappings of 15MgO/SBA-15 showed the homogeneously dispersed Mg species. The FT-IR spectra suggested that a part of Mg species was incorporated into silica walls in the one-pot synthesis method. Also, it was implied that the MgO formation was more prominent as the MgO content increased. The TG analyses indicated a strong interaction between MgO and Mo species,6 it was presumed that CoMo bimetallic catalytic systems are more active than monometallic Co or Mo catalytic systems.9,12 Hence, the incorporation of Mo species may have been another inhibiting factor.
Acknowledgement  This work was supported by JSPS KAKENHI Grant Number JP17H07423.

References
1) Z. A. Alothman, Materials, 5, 2874–2902 (2012).
2) Y. M. Wang, Z. Y. Wu, L. Y. Shi and J. H. Zhu, Adv. Mater., 17, 323–327 (2005).
3) H. V. Lee, J. C. Juan, Y. H. Tauqif-Yap, P. S. Kong and N. A. Rahman, J. Renew. Sustain. Ener., 7, 32701–32746 (2015).
4) S. D. T. Barros, A. V. Coelho, E. R. Lachter, R. A. S. San Gil, K. Dahmouche, M. I. Pais da Silva and A. L. F. Souza, Renew. Energy, 50, 585–589 (2013).
5) B. Huang, X. Li, S. Ji, B. Lang, F. Habimana and C. Li, J. Nat. Gas Chem., 17, 225–231 (2008).
6) J. Scholz, A. Walter, A. H. P. Hahn and T. Ressler, Micropor. Mesopor. Mat., 84, 127–136 (2005).
7) T. E. Bell and L. Torrente-Murciano, Top. Catal., 59, 1438–1457 (2016).
8) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
9) Y. L. Wei, Y. M. Wang, J. H. Zhu and Z. Y. Wu, Adv. Mater., 15, 1943–1945 (2003).
10) B. Li, Z. Xu, F. Jin, S. Luo and W. Chu, Appl. Catal. A-Gen., 533, 17–27 (2017).
11) X. Fu, N. Zhao, J. Li, F. Xiao, W. Wei and Y. Sun, Adsorpt. Sci. Technol., 27, 593–601 (2009).
12) Q. Liu, J. Ma, Y. Zhou and T. Wang, Wuhun Univ. J. Nat. Sci., 19, 111–116 (2014).
13) R. Wang, X. Liu, Y. He, Q. Yuan, X. Li, G. Lu and T. Zhang, Sensor. Actuat. B-Chem., 145, 386–393 (2010).
14) M. Anbia, M. Neyzehdar and R. Dehghan, J. Porous Mat., 20, 217–225 (2017).
15) S. Shen, P. S. Chow, F. Chen and R. B. H. Tan, Chem. Pharm. Bull., 55, 985–991 (2007).
16) I. F. Alexa, M. Ignat, R. F. Popovici, D. Timpu and E. Popovici, Int. J. Pharm., 436, 111–119 (2012).
17) Y. L. Wei, Y. M. Wang, J. H. Zhu and Z. Y. Wu, Adv. Mater., 15, 1943–1945 (2003).
18) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 84, 127–136 (2005).
19) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
20) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
21) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
22) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
23) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
24) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
25) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
26) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
27) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
28) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
29) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
30) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
31) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).
32) Y. M. Wang, Z. Y. Wu, Y. L. Wei and J. H. Zhu, Micropor. Mesopor. Mat., 170, 130–140 (2012).