The effects of the addition of calcium phosphate on catalytic activities for ammonia decomposition on CoMo-based catalysts

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In this study, wet impregnation method and sol–gel technique were used to prepare CoMo-based catalysts supported on two types of porous silicas containing calcium phosphate. The prepared catalysts were characterized using various techniques, such as N₂ adsorption–desorption measurement, scanning electron microscope, X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), differential thermal analysis, and X-ray photoelectron spectroscopy. The catalysts were tested for ammonia decomposition to produce CO₂-free hydrogen. The results of the XRD and FT-IR measurements elucidated that the crystal structure of calcium phosphate on the silica supports was attributed to calcium hydroxyapatite (HAp). The addition of calcium phosphate changed the porous structures of the catalysts, and decreased their BET surface areas and total pore volumes. Furthermore, the catalytic activity of the CoMo-based catalysts was influenced by the amount of calcium phosphate added. It was observed that the ammonia conversion at 873 K was increased by a maximum of 12.6 % when 0.5 wt% of calcium phosphate was added to the catalyst, while a further addition of calcium phosphate beyond 1.0 wt% inhibited the ammonia conversion. From this study, it was concluded that HAp could work as a promoter for ammonia decomposition.

Key-words : Ammonia decomposition, Hydrogen carrier, Porous silica, Calcium hydroxyapatite, Cobalt-molybdenum nitride

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1. Introduction

Hydrogen is a clean and sustainable energy source which can be utilized in fuel cells to produce electricity with a high energy efficiency.¹ However, due to its low volumetric energy density and the difficulty in its storage and transportation, the widespread application of hydrogen has been hampered. To overcome the barriers to the usage of hydrogen-powered devices, it is reasonable to utilize a hydrogen carrier since the densification of hydrogen requires a very high pressure conditions.² Among various hydrogen carrier candidates, ammonia is the most preferred because of the following: (i) It can be liquefied at room temperature at under 1 MPa.³ In addition, the infrastructures for mass production and transportation of ammonia has already been established. These features lead to savings in production, storage, and transportation of hydrogen. (ii) It has high energy and hydrogen density.⁴ (iii) Its flammable range in air (16–25 vol.%) is narrower than that of hydrogen (4–75 vol.%).⁵ Moreover, the energy necessary for the dehydrogenation of ammonia is potentially much lower than that required for methycyclohexane, which is another feasible hydrogen carrier.

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To date, various catalysts for ammonia decomposition have been investigated. Although ruthenium (Ru) is known as one of the most active species, Ru-based catalysts are not desirable for mass utilization owing to their poor availability and high cost.² For the development of inexpensive and highly active catalysts for ammonia decomposition, metals, bimetals, carbides, and nitrides such as Fe⁶–⁹,¹¹–¹⁴ Co⁸,¹²,¹³,¹⁴,¹⁵ Ni,¹,⁸,¹¹,¹⁴,¹⁶ FeCo,¹⁷ NiFe,¹⁸ Mo₂C,¹⁹ Mo₂N,²⁰ MoN,²¹ Ni₃Mo₂N,²² Co₃Mo₂N,²₃,²⁰ and MnN–Li₂NH,²³–⁴¹ have been investigated as active species for ammonia decomposition. Among these, Co₃Mo₂N is one of the most promising catalysts as an inexpensive and highly active catalyst since its binding energy with nitrogen is suitable for ammonia decomposition. The binding energy is a crucial factor for the catalytic activity since it affects the rate of the associative desorption of nitrogen, which is the rate-limiting step (i.e., the slowest step in the chemical reaction that determines the overall rate) of ammonia decomposition.³,¹⁶ Hence, CoMo-based catalysts were prepared by using microporous and mesoporous silicas as supports in this research.

In addition to active species, a promoter can also be used to improve the catalytic activity. To date, alkali and alkaline earth metals, transition metals, and rare earth metals have been investigated as promoters for ammonia decomposition.¹,³,⁷,⁹,¹¹,¹³,¹⁴,¹⁶,¹⁸,¹⁹,²³–⁴¹
decomposition.\(^{2,12,24-29}\) It is believed that the electron donating ability of the promoters contributes to the acceleration of the catalytic activity for ammonia decomposition because a high electron density of the active species can facilitate the associative desorption of nitrogen by donating the electron to the chemically adsorbed nitrogen.\(^{30}\) In this study, calcium hydroxyapatite, a form of calcium phosphate \([\text{HAp}, \text{Ca}_{10}(\text{PO}_4)_{6}(\text{OH})_2]\), was used as a novel promoter for a \(\text{CoMo}\)-based catalyst to decompose ammonia. HAp possesses \(\text{Ca}^{2+}\) sites surrounded by \(\text{PO}_4^{3-}\) tetrahedra parallel to the hexagonal axis, which have the potential to be a biomaterial, an adsorbent, and an ion exchanger.\(^{31}\) Hence, HAp has the structural flexibility, and the \(\text{Ca}^{2+}\) and \(\text{PO}_4^{3-}\) ions in its structure can be replaced by various kinds of cations and anions.\(^{32,33}\) More interestingly, it has been reported that free radicals are generated and trapped on the vacancy of HAp at a relatively high temperature.\(^{34}\) Ammonia decomposition, being an endothermic reaction, often takes place at above 673 K. Hence, it is estimated that free radicals are generated under this reaction temperature and it is expected that the free radicals of HAp which are generated during the reaction can contribute to the electron donation to the active species. In addition, it has been proposed by Wang et al. that the HAp nanotube provides the TiO2-based catalyst with electron and promotes the hydrodesulfurization reaction at 553 K.\(^{35}\) However, to the best of our knowledge, there is no report on the application of HAp as a promoter to a catalyst for ammonia decomposition, in spite of its unique characteristics. Here, the effects of the addition of calcium phosphate (i.e., HAp) to CoMo-based catalysts on their catalytic activities were investigated.

2. Experimental procedures

2.1 Materials

Tetraethoxysilane \([\text{C}_2\text{H}_5\text{O}]_4\text{Si}; \text{TEOS}, 98\%\), 28\% aqueous ammonia (\(\text{NH}_3\)), calcium nitrate tetrahydrate \([\text{Ca(NO}_3)\text{2}·4\text{H}_2\text{O}, 98.5\%]\), phosphorous oxide \((\text{P}_2\text{O}_5, 97\%\)), cobalt nitrate hexahydrate \([\text{Co(NO}_3)\text{2}·6\text{H}_2\text{O}, 98\%]\), hexaammonium heptamolybdate tetrahydrate \([\text{(NH}_4)_6\text{Mo}_7\text{O}_{24}·4\text{H}_2\text{O}, 99\%]\), and potassium bromide (KBr, 99\%) were purchased from Tokyo Chemical Industry Co., Ltd. Acetone (99.5\%), 35\% hydrochloric acid (HCl), acetic acid (99.5\%), and sulfuric acid (97\%) were purchased from Kishida Chemical Co., Ltd. Ethanol (99.5\%) was purchased from Amakasu Chemical Industries Co., Ltd. Cetyltrimethylammonium bromide (CTAB, 98\%) was purchased from Tokyo Chemical Industry Co., Ltd. Carbon black (CB) was purchased from Sigma-Aldrich Japan, Inc. All chemicals were used as-received without further purification.

2.2 Catalyst preparation

Microporous silica (denoted as \(\mu\)-SiO2) was prepared by slightly modifying a previously reported method\(^{36}\) as follows: First, 50 mL of TEOS was dissolved in 50 mL of acetone. Then, 0.1 M aqueous HCl was prepared by diluting 35\% aqueous HCl with deionized water. Next, 1 mL of 0.1 M aqueous HCl, 16 mL of deionized water, and 16 mL of acetic acid were mixed together and added to the above silica precursor solution. This mixed solution was stirred at room temperature until its gelation (gel transition) was completed. Subsequently, the gel was crushed, washed with ethanol, centrifugated, and dried in air. Finally, \(\mu\)-SiO2 was obtained by calcining the dried sample at 773 K for 3 h.

Mesoporous silica (denoted as m-SiO2) was also prepared by slightly modifying a previously reported method\(^{37}\) as follows: First, 13.4 g of CTAB was added to 557.7 g of deionized water. Then, the solution was stirred for 5 min. After that, 220.9 g of ethanol was added to the solution and it was stirred for 5 min. Then, 60.2 g of 28\% aqueous NH3 was added and it was stirred for 5 min. Finally, 18.7 g of TEOs was added to the above and this resulted in a white precipitate within 10 min. After stirring it for 4 h, the white precipitate was filtrated, washed with deionized water, and dried in air. Finally, m-SiO2 was obtained by calcining the dried sample at 823 K for 4 h.

HAp was formed on the surfaces of the silica supports by the previously reported sol–gel technique\(^{38}\) with a slight modification. Here, 2 g of \(\mu\)-SiO2 or m-SiO2 was introduced to ethanol containing \(\text{Ca(NO}_3)\text{2}·4\text{H}_2\text{O}\) and \(\text{P}_2\text{O}_5\) at a Ca to P stoichiometric ratio of 1.67. To obtain solutions with 0.5–20 wt\% of HAp, the amounts of \(\text{Ca(NO}_3)\text{2}·4\text{H}_2\text{O}\) and \(\text{P}_2\text{O}_5\) were adjusted. After adding \(\mu\)-SiO2 or m-SiO2 to the solution, the solution mixture was stirred at room temperature until the ethanol evaporated. The resulting products were dried in air at 313 K and subsequently calcined at 1073 K for 5 h at a heating rate of 3 K/min. The obtained silica-supported calcium phosphates were denoted as \(x\text{CaP}/\mu\)-SiO2 \((x = 0.5, 1, 5, 10, \text{or} 20)\) and \(y\text{CaP}/m\)-SiO2 \((y = 0.5, 1, 5, \text{or} 10)\), in which \(x\) and \(y\) represent the weight percentage of calcium phosphate, which is assumed to be in the form of HAp crystals. Bulk calcium phosphate (denoted as CaP), which would serve as a control sample, was also synthesized by the same procedure without the addition of the silica powders. Impregnation of Co and Mo was conducted by a wet impregnation method using an aqueous solution of \(\text{Co(NO}_3)\text{2}_2\) and \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\). In the present study, the total content of Co and Mo and the Co/Mo molar ratio were adjusted to 5.0 wt\% and 1.0, respectively.

2.3 Characterization

The Brunauer–Emmett–Teller (BET) surface area,\(^{39}\) the total pore volume, and the average pore diameter were obtained by \(\text{N}_2\) adsorption–desorption measurement at 77 K (BELmax-II, MicrotracBEL Corp.). Prior to the measurements, the catalysts were evacuated at 573 K for 3 h. The micropore volume and the pore size distribution were obtained by analyzing the \(\text{N}_2\) adsorption–desorption isotherm via the Barrett, Joyner, and Halenda (BJH) method\(^{40}\) and the t-plot\(^{41}\) respectively. The morphologies of the catalysts were observed by scanning electron microscope (SEM; S-4800, Hitachi High-Tech Science Corp.). X-ray diffraction (XRD) patterns were collected on an X-ray...
diffraetometer (Smartlab, Rigaku Corp.) using monochromatized Cu Kα radiation (λ = 0.15418 nm). In addition to XRD, the crystal structures of calcium phosphates on the silica supports were confirmed by using a fourier-transformed infrared (FT-IR) spectrometer (Vertex 70, Bruker Corp.) by KBr method. The electron donating ability of each sample was evaluated via differential thermal analysis (DTA) measurement (EXSTAR6000, SII Nano Technology Inc.). Prior to the DTA measurements, samples were physically mixed with CB by grinding them in an agate mortar. CB contents of all samples were adjusted to 20 wt%. The DTA measurements were performed under 100 mL/min of air flow with a heating rate of 5 K/min from room temperature to 1073 K. Chemical states of Mo and Co were estimated by an X-ray photoelectron spectroscopy (XPS) equipped with monochromatic 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 (0.4 g) was pelletized 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 the active species. After the pretreatment, the catalytic activity test was started by streaming 40 mL/min of NH₃ gas with a heating rate of 5 K/min of air flow at atmospheric pressure. The reaction temperature was increased from 773 to 973 K in steps of 50 K. At each step, the temperature was kept constant for 15 min. After the unreacted NH₃ gas was trapped with a sulfuric acid solution, the total of the produced gases was measured. The conversion of ammonia was calculated from the flow rates of inlet and outlet gases, which were denoted as \( F_{\text{in}} \) and \( F_{\text{out}} \) respectively.

3. Results and discussion

3.1 Microstructures

\( \text{N}_2 \) adsorption–desorption isotherms and the textural properties of the catalysts are shown in Fig. 1 and Table S1. The isotherm of \( \mu\)-SiO₂ was classified as type I according to the International Union of Pure and Applied Chemistry (IUPAC) classification, indicating the existence of micropores [Fig. 1(a)]. On the contrary, m-SiO₂ showed a typical type IV isotherm which originates from a highly ordered mesoporous structure [Fig. 1(b)]. As summarized in Table S1, the BET surface areas and the total pore volumes of the silica supports decreased after the addition of calcium phosphate. It may be observed that the significant reductions in the BET surface area and the total pore volume in the case of \( \mu\)-SiO₂ were caused by the blockage of the narrow micropores with calcium phosphate. Furthermore, the peak of the pore size distribution of \( \mu\)-SiO₂ at about 1.4 nm almost disappeared when more than 1.0 wt% of calcium phosphate was present, while it remained when less than or equal to 1.0 wt% of calcium phosphate was present [Fig. 1(c)]. The disappearance of the peak was mainly caused by the decrease in the total pore volume due to the blockage of the original micropores as stated above. On the other hand, m-SiO₂ showed a sharp peak at 2.2 nm, indicating the ordered mesostructure [Fig. 1(d)]. However, its peak intensity weakened and its peak position shifted to ca. 1.3 nm. This was presumably caused by the partial destruction of the mesostructure, the coating with calcium phosphate on the mesopores, and/or the thermal shrinkage of the mesopores during the calcinations.

As shown in Figs. 2 and S1, the morphologies of the prepared samples were observed by SEM. The sizes of \( \mu\)-SiO₂ particles were larger than those of m-SiO₂ particles, and furthermore, their shapes were irregular. Therefore, it was difficult to distinguish calcium phosphate particles from the original \( \mu\)-SiO₂ particles (Fig. S1). On the other hand, m-SiO₂ particles were relatively homogeneous in size and roughly spherical in shape (Fig. 2). Therefore, rod-like particles of 1CaP/m-SiO₂ and 10CaP/m-SiO₂ could be distinguished and observed on the external surface of the m-SiO₂ particles [Figs. 2(b) and 2(c)]. However, the number of rod-like particles observed for 1CaP/m-SiO₂ was much less than that observed for 10CaP/m-SiO₂. Those particles were considered to be HAp because an HAp crystal is hexagonal in shape. Hence, these results implied that a part of the calcium phosphate precursor did not fill into the mesopores and HAp formed on the external surfaces of m-SiO₂ particles, especially at a calcium phosphate content of 10 wt%. However, the calcium phosphate precursor seemed to preferentially fill the micropores or mesopores since the BET surface areas and
the total pore volumes decreased with increasing calcium phosphate content (Table S1).

3.2 Crystal and ordered mesoporous structures

As shown in Fig. 3(a), the crystal structure of the obtained bulk calcium phosphate, CaP, was mainly identified as HAp (PDF#01-071-5048). However, no peaks due to calcium phosphates were detected in CaP/¯SiO2 when the amount of calcium phosphate was less than or equal to 5.0 wt% of calcium phosphate. When higher than 5.0 wt% of calcium phosphate was added, the peaks due to HAp appeared and their intensities increased. Considering the increasing tendency of the peak intensities due to HAp, calcium phosphates in 1CaP/¯SiO2 and 5CaP/¯SiO2 were also estimated to be HAp. When using m-SiO2 as a support, no peaks due to calcium phosphates were detected for CaP/m-SiO2 even at 10 wt% of calcium phosphate [Fig. 3(c)]. This was probably because its highest BET surface area aided the dispersion of calcium phosphate (Table S1).

After the impregnation of Co and Mo, the peaks due to HAp in CoMo/CaP/µ-SiO2 and CoMo/CaP/m-SiO2 at about 32° were intensified during the calcinations [Figs. 3(b) and 3(d)]. Although the peaks due to CoMoO4 were detected at about 26° (PDF#00-021-0868) for CoMo/CaP/µ-SiO2 and CoMo/CaP/m-SiO2, their intensities weakened with the addition of 10 wt% of calcium phosphate. It is known that Ca2+ ions of HAp can exchange with various cations including Co2+ ions.32) Therefore, this ion-exchange ability may have inhibited the Co and Mo precursors from forming CoMoO4 with 10 wt% of calcium phosphate.

XRD patterns at low diffraction angle were also recorded for the m-SiO2-supported catalysts [Fig. 3(e)]. Three peaks detected were assignable to 100, 110, and 200 planes of diffraction from the hexagonally ordered mesoporous structure.43) According to a previously reported study,37) the cubic mesoporous structure should have been obtained using the present preparation procedure. The differences in the preparation conditions such as the stirring speed of the magnetic stirrer and the ambient temperature might have induced the hexagonally ordered mesoporous structure in the present study. Furthermore, the first peak assigned to 100 plane of diffraction remained even after the

![Fig. 2. SEM images of (a) m-SiO2, (b) 1CaP/m-SiO2, and (c) 10CaP/m-SiO2.](image)

![Fig. 3. XRD patterns of the fresh samples at (a–d) high diffraction angle and (e) low diffraction angle.](image)
CaP and CoMo impregnation, although the intensity was weakened. Therefore, it was inferred that the ordered structure partially remained even after the CaP and CoMo impregnation. At the same time, it was also confirmed that the first peak shifted to a higher angle after CaP and CoMo impregnation. This was presumably caused by the thermal shrinkage of the mesopores during the calcinations at 1073 and 773 K.

In addition to the XRD patterns, FT-IR spectra were recorded for CaP/\(\mu\)-SiO\(_2\), CaP/m-SiO\(_2\), and CaP in order to confirm the crystal structure of calcium phosphate supported on \(\mu\)-SiO\(_2\) and m-SiO\(_2\) (Fig. 4). The absorption bands at approximately 460, 803, and 1090 cm\(^{-1}\) were ascribed to Si–O–Si stretching vibration\(^{38,44}\). The absorption bands of CaP at 572 and 602 cm\(^{-1}\), 1044, and 1090 cm\(^{-1}\) were considered to belong to \(\nu_4(PO_4)^{3-}\) and \(\nu_3(PO_4)^{3-}\), respectively.\(^{38}\) Since these absorption bands could be attributed to HAp, the crystal structure of CaP was also considered to be HAp, as confirmed through XRD. The absorption bands of CaP/\(\mu\)-SiO\(_2\) at 572 and 602 cm\(^{-1}\), 1044, and 1090 cm\(^{-1}\) were intensified when the CaP content was increased from 0 to 20 wt% [Figs. 4(b)–4(e)]. However, a weak absorption band at 572 cm\(^{-1}\) was detected only for CaP/m-SiO\(_2\) [Fig. 4(g)]. The highest BET surface area of m-SiO\(_2\) (Table S1) may have caused relatively stronger interaction between calcium phosphate and the silica wall and lowered the absorbance due to HAp. Considering the increase of the absorbance due to HAp, which in turn was due to the increasing calcium phosphate content, it may be speculated that the calcium phosphates supported on \(\mu\)-SiO\(_2\) and m-SiO\(_2\) are HAp even at low calcium phosphate content.

### 3.3 Catalytic activities

Two moles of ammonia can be decomposed to 1 mol of nitrogen and 3 mols of hydrogen (\(2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2\)). Therefore, ammonia conversion of each catalyst was calculated by following equation, NH\(_3\) conversion (%) = \((F_{\text{out}}/2F_{\text{in}}) \times 100\), assuming that the produced gas was composed of nitrogen and hydrogen. Therefore, selectivity to hydrogen is assumed to be constantly 100% in this reaction. Figure 5 shows the catalytic activities of the CoMo-based catalysts. Their ammonia conversions were increased because of the rising reaction temperature owing to the endothermicity of ammonia decomposition. The catalytic activity of CoMo/\(\mu\)-SiO\(_2\) was higher than that of CoMo/m-SiO\(_2\), in spite of having a lower BET surface area (Table S1). Therefore, a narrower pore size and/or randomly distributed pore channels of a catalyst may be more favorable than 1D mesoporous channels for ammonia decomposition under the present reaction conditions. The positive promoting effects of HAp were confirmed by adding small amounts of calcium phosphate. As summarized in Table 1, the apparent activation energies of CoMo/\(\mu\)-SiO\(_2\) and CoMo/m-SiO\(_2\) decreased by adding 1.0 wt% of calcium phosphate. Although the metal contents of our catalysts were the lowest among the listed catalysts, their apparent activation energies were estimated to be relatively low in comparison with the other catalysts.\(^{6,12,20,21}\)

Furthermore, the ammonia conversion of CoMo/m-SiO\(_2\) increased by 12.6% at 873 K by adding 0.5 wt% of...
Table 1. Apparent activation energies of the various catalysts for ammonia decomposition

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Apparent activation energy (kJ mol⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoMo/µ-SiO₂</td>
<td>82</td>
<td>This study</td>
</tr>
<tr>
<td>CoMo/1CaP/µ-SiO₂</td>
<td>76</td>
<td>This study</td>
</tr>
<tr>
<td>CoMo/m-SiO₂</td>
<td>92</td>
<td>This study</td>
</tr>
<tr>
<td>CoMo/1CaP/m-SiO₂</td>
<td>82</td>
<td>This study</td>
</tr>
<tr>
<td>Ca₁₀₋₂₀Co₂Mo₃N</td>
<td>65.1</td>
<td>6)</td>
</tr>
<tr>
<td>7 wt% Co/AX-21</td>
<td>88.74</td>
<td>12)</td>
</tr>
<tr>
<td>3CoMoN</td>
<td>92.8</td>
<td>20)</td>
</tr>
<tr>
<td>MoN@C</td>
<td>123.8 ± 2.4</td>
<td>21)</td>
</tr>
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</table>

calcium phosphate, while that of CoMo/µ-SiO₂ increased by only 2.4% at 873 K under the same conditions. These different promoting effects may be related to the difference in the porous structures. As mentioned above, the N₂ adsorption–desorption isotherm of m-SiO₂ changed from type IV to type I after the addition of calcium phosphate, decreasing its pore diameter and increasing its micropore volume (Fig. 1 and Table S1). Hence, the promoting effects of HAp and the change in the porous structure of m-SiO₂ were the likely contributors to the enhanced catalytic activity. On the contrary, the ammonia conversions of CoMoO₄ decreased from 23.4 and 14.1% at 873 K, respectively, with the addition of 10 wt% of calcium phosphate. Therefore, CoMo/10CaP/m-SiO₂ exceeded CoMo/10CaP/µ-SiO₂ in ammonia conversion (Fig. 5). This is presumably because the blockage of the micropores of µ-SiO₂ with calcium phosphate caused the decrease in the BET surface area and the total pore volume (Table S1). The lowest catalytic activity of CoMo/CAp could be ascribed to the lowest BET surface area of CaP (7.7 m²/g) and the greater ion-exchange ability with Co²⁺ ions.

As stated above, the donation of electrons by a promoter to the active species can improve the catalytic activity for ammonia decomposition. Hence, the electron-donating effects of calcium phosphates were elucidated via DTA measurement. In this measurement, a combustible behavior of CB was assumed to be related to the electron-donating ability of HAp since free radicals generated on its surface at a relatively high temperature could activate oxygen and promote the combustion of organic compounds. Figure 6 shows the combustible behavior of CB physically mixed with each sample. As shown in the figure, the combustion temperatures were CaP < 10CaP/µ-SiO₂ ≈ 10CaP/m-SiO₂ < µ-SiO₂ ≈ m-SiO₂. In contrast, the peak areas which reflect the combustion heats were µ-SiO₂ ≈ m-SiO₂ < 10CaP/µ-SiO₂ ≈ 10CaP/m-SiO₂ < CaP. As stated above, 10CaP/µ-SiO₂ and 10CaP/m-SiO₂ have rod-like HAp particles on the external surfaces. These results indicate that HAp possessed the relatively strong oxidative decomposition ability. Therefore, it was considered that the promotion of combustion of CB could be ascribed to the reactive oxygen species which were produced by the electron donation from free radicals on HAp. This electron donation of HAp might have contributed to the enhancement of the catalytic activities as shown in Fig. 5.

3.4 Catalyst characterization after the reaction

As shown in Fig. 7, the XRD patterns of the catalysts after the catalytic activity testing were collected. It can be inferred that CoMoO₄ changed to Co₃Mo₃N after the reaction (PDF#01-089-7953). It is considered that the above phase transitions occurred during the pretreatment with ammonia at 973 K because the Arrhenius plots of the catalysts was almost linear (Fig. S2). The linear Arrhenius plots imply that the catalysts showed the stable activities without significant phase transitions during the catalytic activity testing. For CoMo/CAp/m-SiO₂, the peak intensities of CoMoO₄ and Co₃Mo₃N increased from 0 to 5.0 wt% of calcium phosphate [Figs. 3(d) and 7(b)]. However, those intensities weakened with the increase of calcium phosphate from 5.0 to 10 wt%. As mentioned above, HAp can promote the ion-exchange of Ca²⁺ ions with Co²⁺ ions. Hence, it may be presumed that a part of Co and Mo species could not be transformed to CoMoO₄, leading to the formations of γ-Mo₂N and metallic Co as stated below. On the other hand, the peak intensities of Co₃Mo₃N of CoMo/CAp/m-SiO₂ increased as calcium phosphate content increased from 0 to 10 wt% [Fig. 7(a)]. The drastic decrease in the BET surface area (Table S1) may have dominantly influenced the growth of Co₃Mo₃N phase over the ion-exchange ability of HAp.

Figures 8(a)–8(c) show XPS spectra of CoMo/m-SiO₂, CoMo/1CaP/m-SiO₂, and CoMo/10CaP/m-SiO₂ after ammonia decomposition. According to the previous reports, the peaks located at 228.3 and 232.4 eV corresponded to Mo²⁺/³⁺ (2 < δ < 4) and Mo⁶⁺ in Mo3δ/2, respectively. For all the catalysts, the main peaks were positioned at approximately 232.4 eV, indicating higher oxidation states of Mo species such as Mo⁶⁺, which Co₃Mo₃N is mainly composed of. In addition to the main peaks, a weak peak at approximately 228.7 eV was observed for CoMo/10CaP/m-SiO₂. The weak peak at ca. 228.8 eV can be attributed to the isolated γ-Mo₂N, which is mainly composed of Mo²⁺ and Mo⁶⁺ (2 < δ < 4).
As discussed above, these results also indicated that a part of the Co and Mo species could not form CoMoO$_4$ which is a precursor of Co$_3$Mo$_3$N. With respect to the XPS spectrum of Co 2p$^{3/2}$, it was considered that the two broad peaks at 782 and 787 eV represented the existence of Co$^{3+}$ and Co$^{3+}$, which Co$_3$Mo$_3$N is mainly composed of. In addition to the above broad peaks, a weak peak at about 778 eV was observed for CoMo/10CaP/m-SiO$_2$. This weak peak may represent the existence of Co$^0$ species.

As mentioned above, the BET surface areas and the catalytic activities decreased when greater than 1.0 wt% of calcium phosphate was added. Furthermore, excessive doping of calcium phosphate was likely to suppress the formation of catalytically active Co$_3$Mo$_3$N. In contrast, the addition of 0.5 and 1.0 wt% of calcium phosphate promoted ammonia decomposition on the CoMo-based catalysts without a significant decrease in the BET surface area and isolations of Co and Mo species. According to a previous report, the addition of CeO$_2$ enhanced the catalytic activity of Ni/Al$_2$O$_3$ for ammonia decomposition. Furthermore, it has been speculated by Zheng et al. that the promoting effects of CeO$_2$ are ascribed to mobile electrons in the oxygen anion vacancy on the CeO$_2$ surface. In spite of the lack of a mixed valence state like Ce$^{3+}$/Ce$^{4+}$, it is observed from the results of the DTA measurements that free radicals can be generated and trapped at the vacancy of HAp at a relatively high temperature. Hence, the observed promoting effects of HAp in the present catalytic system may also be attributed to the electron-donating ability of the free radicals generated under the reaction conditions.

4. Conclusions

Calcium phosphate was investigated as a promoter for CoMo-based catalysts. The addition of calcium phosphate changed the porous structures of μ-SiO$_2$ and m-SiO$_2$, and decreased their BET surface areas and total pore volumes. Furthermore, it was observed from the XRD and FT-IR measurements that their crystal structures could be attributed to HAp. The addition of 0.5 or 1.0 wt% of calcium phosphate enhanced the catalytic activities of CoMo/μ-SiO$_2$ and CoMo/m-SiO$_2$. Hence, it was revealed that HAp can work as a promoter for ammonia decomposition. From the results of the XRD measurements, it can be inferred that CoMoO$_4$ of the fresh catalysts was transformed to Co$_3$Mo$_3$N during the pretreatment with ammonia at 973 K. The results of the DTA measurements suggested that the generation of the free radicals on the surfaces of CaP, 10CaP/μ-SiO$_2$, and 10CaP/m-SiO$_2$ at a relatively high temperature. The positive promoting effects of calcium phosphate may be related to the electron-donating ability of free radicals that are generated under the reaction conditions. On the other hand, the addition of greater than 1.0 wt% of calcium phosphate inhibited the catalytic activities.
This inhibiting effect can be ascribed to the decrease in the BET surface area, the pore volume, and the likelihood of the formation of a Co3Mo3N phase which is the catalytically active phase for ammonia decomposition.

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Appendix A. Supporting information Supplementary data associated with this article can be found in the online version.

References