FULL PAPER

Preparation of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ -based porous hybrid with Ru for H_2 generation catalyst by NH_3 decomposition

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Layered calcium niobate perovskite with partial substitution of Nb by Ru was prepared for the catalyst of H_2 generation from NH_3 . The X-ray photoelectron spectroscopy confirmed that the substituted Ru exists at the intralayer position. The layered perovskite was exfoliated and re-aggregated with Ru and Na cation to increase the surface area to form a card house-type porous hybrid. The surface area apparently increased to around 12–18 times compared to the sample without exfoliation. The amount of interlayer Ru is much larger than that of the intralayer Ru from the X-ray fluorescence measurement. From the H_2 generation measurements, different roles of the intralayer and interlayer Ru were considered as follows. The interlayer Ru lowers the starting temperature of the H_2 generation, whereas the intralayer Ru increase the H_2 generation rate.

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1. Introduction

Currently, energy issues are being discussed from various viewpoints such as global warming and environmental pollution, and new clean energy that can provide a stable supply with less loading on the environment is required.^{1)–4)} Therefore, hydrogen has been attracting attention as new energy. The use of the hydrogen generally generates the water which is the most stable product of the compound produced from hydrogen and oxygen without emission of substances related to environmental issues such as carbon dioxide. Also, in combination with fuel cell technology, the very high energy conversion efficiency can be obtained. Further, since hydrogen is contained in various substances, there is no fear of depletion and so on. For these reasons, hydrogen may be only one material as the most important secondary energy source in the future.^{5)–10)} In recent years, a fuel cell vehicle and a home fuel cell with hydrogen as an energy source have been used widely.^{11)–13)} In this way, hydrogen will become widespread in the energy field. Therefore, it is necessary to research the production and storage method of hydrogen with high efficiency for the futural hydrogen energy-based society.

Ammonia is a promising candidate as a carrier material for hydrogen. The first reason is no carbon. Thus, only hydrogen and nitrogen are generated during the decom-

position of the ammonia in the inert atmosphere. Therefore, it can be used as a carrier in the carbon-free hydrogen storage and transport system. The second reason is the very high hydrogen content density in ammonia (75 atom %, 17.6 wt %).^{6),8),11),14),15)} However, there is no efficient way to decompose ammonia into hydrogen and nitrogen, so the utilization of ammonia as a hydrogen carrier is limited. To extract hydrogen from ammonia, heat treatment for the decomposition of the ammonia under a catalyst existence is known as a general process. The reaction is represented by the following chemical formula.^{1),16)}

From this formula, decomposition is found to be an endothermic reaction. Besides, the thermal tendency for free energy change can be calculated from the temperature dependence of the standard enthalpy of formation and standard entropy. From this calculation, the decomposition of ammonia should proceed at a temperature of about 185 °C or higher thermodynamically because the free energy change will be negative.¹⁷⁾ However, the actual decomposition temperature is around 600 to 800 °C. Since such high temperature spends a lot of time and energy, research and development of highly active catalysts that can be decomposed at lower temperatures are being conducted.

The layered perovskite has a layered structure in which an octahedral structure is two-dimensionally connected to form perovskite slab and an alkali or an alkaline earth metal cation is intercalated between these slabs. Layered perovskites are classified into three types, Dion-Jacobson type $\text{A}'[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$, Aurivillius type $(\text{Bi}_2\text{O}_2)[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$,

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and Ruddlesden–Popper type $A'_2[A_{n-1}B_nO_{3n+1}]$, depending on their structure.¹⁶⁾ Generally, the layered perovskites have a large degree of freedom in composition within the perovskite slab and can perform an ion exchange reaction of alkali metal ions between the slabs and an intercalation reaction for introducing ions or molecules between these slabs. Furthermore, these materials can be exfoliated into nanosheets, and the nanosheets can be laminated. These features are expected to be applied in many fields.^{17)–21)}

In this study, $KCa_2Nb_3O_{10}$, a Dion–Jacobson type of layered perovskite, is used as an ammonia decomposition catalyst. This compound is partially substituted with Ru, which has been reported to be effective for ammonia decomposition activity.^{5),6),9),11)} Further, basing on the characteristics of the layered compound, the alkali metal ions are exchanged for protons, the layered structure exfoliated to form nanosheets, Ru adheres to the nanosheets, and then re-lamination is performed to increase the porosity or the specific surface area. These processes aim to improve ammonia decomposition activity.

2. Experimental procedure

2.1 Preparation of layered perovskites

The layered perovskites were prepared via conventional solid-state reactions with heating at a high temperature. For the preparation of $KCa_2Nb_3O_{10}$, a mixed powder composed of K_2CO_3 , $CaCO_3$, and Nb_2O_5 in a molar ratio of 1.2:4.0:3.0 was heated at 1100 °C for 48 h.

To synthesize a product with partial substitution by Ru for Nb, raw materials, K_2CO_3 , $CaCO_3$, Nb_2O_5 , $BaCO_3$, and $RuCl_3 \cdot nH_2O$ were mixed with the ratio of 1.2(1 – x):4.0:3.0(1 – x):3.0x:3.0x, and it was heated at 1100 °C for 48 h. Here, Ba was added for charge compensation for the substitution of Ru^{4+} for Nb^{5+} . The additive concentration x was set at 0.0083 and 0.0167. The heated samples of $KCa_2Nb_3O_{10}$ are designated the abbreviations KCN(100x).

Next, the heated samples were then added to 1 M HNO_3 aqueous solution for protonation; the K ions were exchanged with H ions by shaking the mixtures for 5 days in the acid solution which was replaced daily. The treated sample was separated and washed by centrifugation, and was dried at 50 °C. The protonated samples are designated as HCN(100x), hereafter.

2.2 Exfoliation of the compounds and deposition of Ru onto nanosheets

Tetrabutylammonium hydroxide (TBAOH) was reacted with the protonated layered perovskites. The protonated perovskites, HCN(100x), were added to TBAOH aqueous solution with a concentration of 64 mmol/L and shaken for 1 week to be exfoliated by the addition of TBA cations. The ratio of the TBA cation and the perovskite were set to 8.

Next, the colloidal suspension of exfoliated perovskite nanosheets was added into a mixed solution of water and methanol, into which $RuCl_3 \cdot 3H_2O$ had been dissolved with a concentration of 20 mmol/L. The dissolved amount corresponded to 0.67 at % Ru for $HCa_2Nb_3O_{10}$. The obtained sample is called ex-HCN(100x)-Ru.

Thereafter, 54.5 mL of a 2.0 M NaOH aqueous solution was added dropwise little by little. Solid–liquid separation and washing were performed by centrifugation and was dried at 50 °C.

2.3 Catalytic reaction of ammonia decomposition

Hydrogen generation from an ammonia gas was performed as follows: The sample was placed in a silica glass tube with 1 cm in diameter and silica wool was placed to fix it. The sample was heated while flowing a mixed gas of ammonia and argon (ammonia 5 %) at a rate of 10 mL/min in the silica tube. The gas generated in the electric furnace was bubbled in 0.5 mol/L nitric acid to remove excess ammonia. Then, the gas of 1 mL was taken out with a gas-tight syringe and injected into a gas chromatograph (Molecular Sieve-13X column, JASCO) to confirm the amount of generated hydrogen. For the gas chromatography measurement, the column temperature was 50 °C, and the measurement was performed while flowing Ar at 20 mL/min. as a carrier gas.

2.4 Characterization

The structures of the prepared perovskite and their aggregates after exfoliation were identified by an X-ray diffractometer (XRD) with Cu K α radiation monochromatized with a Ni filter (Rigaku, MiniFlex600). The chemical compositions were measured by X-ray fluorescence analysis (XRF, Rigaku ZSX Primus II). The specific surface areas were calculated by BET theory using N_2 isotherms measured at 77 K (BELSORP-mini, MicrotracBEL). Before the measurement, the sample was pretreated by evacuation at 393 K.

Using a field emission scanning electron microscope (FE-SEM), the morphological observation of the reassembly of the partially substituted layered perovskite and nanosheets was performed (JEOL Ltd. JSM6500F). The morphological observation and electron diffraction of the nanosheet was performed using a transmission electron microscope (TEM, JEOL Ltd. TEM2000FX-II).

X-ray photoelectron spectroscopy (XPS) spectra were measured with Al K α radiation (Shimadzu AXIS ULTRA) for the investigation of Ru valence. The coordination state with oxygen was examined using the X-ray absorption fine structure (XAFS) measurement in BL14B2 (SPring-8). In the XAFS measurements, the transmission mode was used passing through a gas flow ion chamber in which He, N_2 , and Ar were automatically supplied to various optimal gas mixtures. The measured data were analyzed by Athena and Artemis.²²⁾

3. Results and discussion

3.1 Preparation of Ru-substituted layered perovskites and soft-chemical reaction

Figure 1 shows the XRD patterns and FE-SEM micrographs of KCN synthesized with each substitution amount of Ru. These XRD patterns confirm that the main phase for all samples is $KCa_2Nb_3O_{10}$. The peaks marked with a filled

Fig. 1. XRD patterns and FE-SEM micrographs of KCN(0), KCN(0.83), and KCN(1.67).

Fig. 2. XRD patterns as-heated, protonated, and exfoliated KCN(0), and KCN(0.83).

circle may be assigned to the impurity phase, K_2RuO_4 . FE-SEM micrographs confirm that each sample has a thin and square shape. In the Ru-substituted sample, some rod-like particles were observed at only KCN(1.67). These particles may indicate the presence of the impurity K_2RuO_4 . From these results, KCN(0.83) was adopted as a partially substituted sample hereafter.

Figure 2 shows the XRD patterns of as-prepared, protonated, and exfoliated KCN(100x) with/without Ru substitution. Here, for the exfoliated samples, XRD measurement was performed by the sample collected by centrifugation. After the protonation, the XRD patterns have slightly changed. These changes may result from a slight change of interlayer distance, the symmetry of crystal structure, and the atomic structural factor, which can be implied as collateral evidence for the protonation. From this result, protonation is probably performed completely.

For the exfoliated samples, the peak at around 6 degrees in two theta eliminated, and a strong peak newly emerged at around 3.6 degrees compared to the protonated sample. This indicates that the interlayer distance was expanded by the intercalation of TBA cations between the layers. Also, these peaks before and after the exfoliation have interlayer spacings of 1.47 and 2.45 nm, respectively. The difference corresponds to the size of the TBA cation of about 1 nm. Therefore, it was considered that a monomolecular TBA layer was formed on the exfoliated nanosheets.

3.2 Structural analysis of porous hybrids

Figures 3(a) and 3(b) show FE-SEM micrographs of the agglomerated nanosheets, ex-HCN(0)-Ru and ex-HCN(0.83)-Ru. Compared to the sample before agglomeration in Fig. 1, the shape and size have changed. Such change results from the exfoliation and agglomeration processes.

Figures 3(c) and 3(d) show TEM micrographs and an electron diffraction image of ex-HCN(0)-Ru. The TEM micrograph (c) shows a nanosheet lying horizontal direction to paper. From the TEM micrographs, some parts with a high contrast of several nm on the nanosheet can be confirmed. These parts are considered to be the deposited Ru. In the electron diffraction image, only spots indicating a single crystal of HCN was observed. From these diffraction spots, the exposed surface of the HCN nanosheet was found to be c-plane. Besides, Ru is possibly ultrafine particles.

Figure 4 shows the Ru3p XPS spectra of KCN(0.83) and ex-HCN(0)-Ru. From these spectra, Ru state substituted within the perovskite structure or deposited on the nanosheet will be expected to be apparent. For KCN(0.83), the peak of Ru 3p_{3/2} apparently be overlapped with a large Nb 3s peak. However, the monomodal Ru 3p_{1/2} peak can be observed, whose binding energy is smaller than that of Ru 3p_{3/2} by 22.2(1)eV.²³⁾ Besides, the

Fig. 3. FE-SEM and TEM micrographs of the exfoliated samples. (a) FE-SEM of ex-HCN(0)-Ru, (b) FE-SEM of ex-HCN(0.83)-Ru, (c) TEM of ex-HCN(0)-Ru, and (d) electron diffraction patterns of ex-HCN(0)-Ru.

Fig. 4. XPS spectra of KCN(0.83) and ex-HCN(0)-Ru.

intensity of 3p_{3/2} should be theoretically 2 times larger than 3p_{1/2}. These restrictions provide the speculative but relatively accurate Ru 3p_{3/2} peak can be separated. Consequently, the separated peak of Ru 3p_{3/2} for substituted Ru in KCN(0.83) seems to be at 465.1 eV. To estimate the chemical state, the energy is compared to the mean Ru 3p_{3/2} binding energies for several RuO₂ and Ru metal phases, which were obtained as 462.7(3) and 461.5(4) eV, respectively, from the NIST XPS database. Resultantly the binding energy is 2.4 and 3.6 eV larger than those of RuO₂ and Ru metal, respectively. These large energy differences imply that the substituted Ru may have a cationic state. If Ru is succeeded to substitute for Nb, the difference is probably due to its coordination state rather than ionic radius. The difference of ionic radius between Nb⁵⁺ and Ru⁴⁺ seems to be too small to affect the chem-

Fig. 5. XAFS spectra of Ru-K absorption edge of exfoliated samples.

ical shift of Ru in the XPS spectrum, considering that the ionic radii are Nb⁵⁺ = 64 pm and Ru⁴⁺ = 62 pm. On the other hand, the coordination environment of MO₆ octahedron is different between NbO₆ in the perovskite structure and RuO₆ in the rutile structure. In other words, when Ru is partially substituted on the Nb site, a RuO₆ octahedron should have a corner-shared structure, whereas a RuO₂ crystal has edge-shared RuO₆ octahedra. The coordination numbers of oxygen to Ru are 2 and 3, respectively. In the rutile structure, oxygen can pull electrons from three Ru cations, but in the perovskite structure, electrons must be pulled from two cations, so Ru became cationic and the binding energy will increase accordingly. This energy shift may be regarded as a collateral proof that Ru was substituted in the B site.

On the other hand, the peak in ex-HCN(0)-Ru, a peak of Ru 3p_{3/2} is observed at around 462.9 eV. From the binding energy of Ru metal and RuO_x as mentioned before, the deposited Ru nanoparticles on the nanosheet are in an oxide state.

Figure 5 shows the XAFS spectra of the Ru-K absorption edge of the exfoliated and re-aggregated samples, ex-HCN(0)-Ru and ex-HCN(0.83)-Ru. The spectrum of KCN(0.83) could not be measured due to the low Ru content by both transmission and fluorescence mode of XAFS. Therefore, the spectrum of only the KCN(0.83) sample cannot be included. It can be seen that both samples have similar spectra and shapes to that of RuO₂. The only difference at a glance among them is peak shape. The peak in RuO₂ is cracked. Since this peak derives from excitation from 1s to 5p orbital, the cracked shape may result from distortion of RuO₆ particularly in the rutile structure. Thus, the non-cracked peak for the samples may indicate the relaxation of the distortion by its ultrafine size. From these considerations, we think the Ru particles on the nanosheet can be regarded as RuO₂ nanoparticle.

Table 1 shows the coordination numbers of ex-HCN(0)-Ru and ex-HCN(0.83)-Ru samples obtained from an analysis of EXAFS omitted in this paper. As mentioned above, the coordination number of KCN(0.83) cannot be calculated because of the very small amount of Ru in the

Table 1. Coordination number and estimated particle size of ex-HCN(0)-Ru and ex-HCN(0.83)-Ru

sample	coordination number	estimated particle size/nm
ex-HCN(0)-Ru	5.4	8.3
ex-HCN(0.83)-Ru	5.0	4.9

Table 2. Specific surface areas of KCN(0), KCN(0.83), ex-HCN(0)-Ru, and ex-HCN(0.83)-Ru

sample	specific surface area/ $\text{m}^2\cdot\text{g}^{-1}$
KCN(0)	0.9
KCN(0.83)	1.0
ex-HCN(0)-Ru	16.3
ex-HCN(0.83)-Ru	12.7

sample. The result of the estimated particle size of RuO_2 particles using this coordination number was also added to the table. These estimated particle sizes were calculated by the following equation.

$$\text{mean CN} = \frac{cn(n_v - n_s) + \frac{cn}{2}n_s}{n_v} \quad (2)$$

Here, mean CN is the average coordination number, cn is the coordination number of Ru to oxygen, n_v is the number of RuO_6 in one particle, and n_s is the number of MO_6 present on the surface of one particle. This calculation assumes that Ru in the particle forms RuO_6 and that on the surface has half the coordination. Thus, cn is fixed at 6. The n_v and n_s are calculated from the volume of RuO_6 octahedron and its cross-sectional area. From this, it is considered that the RuO_x particles exist on the nanosheet with a small size of 10 nm or less.

Table 2 shows the specific surface area calculated by the BET theory. Comparing the specific surface area of the re-agglomerated sample with that before re-agglomeration, it increases by around 12–18 times by performing the exfoliation treatment before the re-aggregation to form the card-house texture as shown in Fig. 3. However, the increase seems to be insufficient for the full exfoliation. Thus, several amounts of nanosheet may be bunched. The schematic illustration of the hybrid model prepared by exfoliation and re-aggregation in this study is shown in **Fig. 6**. The increases in the surface area are expected to accelerate any reaction occurs on the surface; ex some catalytic reactions.

XRF measurements confirmed the amounts of Ru in the hybrids. **Table 3** shows the ratio of Ru and Nb at intra-layer and interlayer positions (Ru_{intra} and Ru_{inter}), which can be provided by the substitution and the re-aggregation process, respectively. From these compositions, the deposited Ru nanoparticles are around 0.7–0.8 times to the Nb by molar ratio, which are much larger than the amount of intralayer Ru substituted for Nb. This is shown as the intensity difference of the XPS spectra in Fig. 4. When the atomic sensitivity factor of Ru 3p_{3/2} may generally be provided, we will be more clear the hybrid structure by

Fig. 6. Schematic illustration of ex-HCN(0.83)-Ru hybrid.**Table 3.** Chemical compositional ratio of Ru and Nb in ex-HCN(0)-Ru and ex-HCN(0.83)-Ru

sample	$\text{Ru}_{\text{intra}}/\text{Nb}$	$\text{Ru}_{\text{inter}}/\text{Nb}$
ex-HCN(0)-Ru	—	0.26
ex-HCN(0.83)-Ru	0.01	0.24

Fig. 7. Temperature dependence of activities of different catalysts for H_2 generation.

comparison of the chemical composition from XPS and XRF measurements in the future. Figure 6 shows the expected schematic illustration of ex-HCN(0.83)-Ru hybrid.

3.3 Catalytic activity

Figure 7 shows the dependence of the H_2 generation amount on temperature. In the blank measurement, the amount of H_2 generated at a temperature from RT to 700 °C was measured without the addition of a catalyst. In all samples, H_2 generation began to increase at lower temperatures compared to blank measurements. In both ex-HCN(0)-Ru and ex-HCN(0.83)-Ru, H_2 generation started above 350 °C. Looking at the conversion degree at 400 °C, ex-HCN(0.83)-Ru show a somewhat larger H_2 amount than ex-HCN(0)-Ru. At 500 °C, the amount of H_2 generation reached larger than 98 % under the existence of ex-HCN(0.83)-Ru sample, whereas that was around 40 % with ex-HCN(0)-Ru. The activity was higher when both partial substitution and re-aggregation were performed. In particular, H_2 generation at high temperatures was improved. Thus, different roles of the intralayer and

interlayer Ru can be considered as follows. The interlayer Ru lowers the starting temperature of the H₂ generation, whereas the intralayer Ru increase the H₂ generation rate. This behavior can be considered by the following two reasons; the different chemical state of Ru as measured by the XPS described above, and the higher diffusion of ammonia at higher the temperature. For the ammonia decomposition at high temperature, the more the diffusion progressed and the ammonia came into contact with the intralayer Ru.

4. Conclusions

We synthesized layered perovskite partially substituted with Ru and prepared layered perovskite hybrid with a relatively high specific surface area. This was intended to improve the ammonia decomposition activity.

In the synthesis of partially substituted layered perovskite, Ru could be substituted for Nb up to 0.83, with simultaneous substitution of K by Ba for the electric compensation. The XPS results showed that the Ru was substituted in the B site.

Moreover, the specific surface area increased to about 12–18 times by exfoliation and re-aggregation of the layered perovskite. The Ru nanoparticles introduced into the hybrid were confirmed to be in an oxide state. When the ammonia decomposition activity of these hybrids was evaluated, the maximum activity was shown in the sample in which Ru was introduced into the intralayer and outside the layers, and the generation of H₂ could be confirmed at 350 °C or higher.

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