


 Cite this: *RSC Adv.*, 2023, **13**, 15410

Facile formation of barium titanium oxyhydride on a titanium hydride surface as an ammonia synthesis catalyst†

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Oxyhydrides are promising compounds as supports for ammonia synthesis catalysts because they suppress hydrogen poisoning on the catalyst surface and enhance the ammonia synthesis activity. Herein, we developed a facile method for preparing BaTiO_{2.5}H_{0.5}, a perovskite oxyhydride, on a TiH₂ surface *via* the conventional wet impregnation method using TiH₂ and Ba hydroxide. Scanning electron microscopy and high-angle annular dark-field scanning transmission electron microscopy observations revealed that BaTiO_{2.5}H_{0.5} crystallized as nanoparticles of ca. 100–200 nm on the TiH₂ surface. The Ru-loaded catalyst Ru/BaTiO_{2.5}H_{0.5}-TiH₂ exhibited 2.46 times higher ammonia synthesis activity (3.05 mmol-NH₃ g⁻¹ h⁻¹ at 400 °C) than the benchmark Ru catalyst Ru-Cs/MgO (1.24 mmol-NH₃ g⁻¹ h⁻¹ at 400 °C) because of the suppression of hydrogen poisoning. The analysis of reaction orders showed that the effect of suppressing hydrogen poisoning on Ru/BaTiO_{2.5}H_{0.5}-TiH₂ was equivalent to that of the reported Ru/BaTiO_{2.5}H_{0.5} catalyst, thus supporting the formation of BaTiO_{2.5}H_{0.5} perovskite oxyhydride. This study demonstrated that the selection of appropriate raw materials facilitates the formation of BaTiO_{2.5}H_{0.5} oxyhydride nanoparticles on the TiH₂ surface using the conventional synthesis method.

 Received 8th March 2023
 Accepted 17th May 2023

DOI: 10.1039/d3ra01539d

rsc.li/rsc-advances

Introduction

Ammonia (NH₃), an essential raw material in the production of agricultural fertilizers and synthetic chemicals, has recently attracted attention owing to its applicability as a hydrogen carrier or fuel.^{1,2} Ammonia is predominantly produced *via* the Haber–Bosch (HB) process, which accounts for 1–2% of the global energy demand and 2.5% of global CO₂ emissions.³ Most of the CO₂ emissions are responsible for hydrogen production processes using steam reforming (CH₄ + H₂O → CO + 3H₂) and water gas shift reactions (CO + H₂O → CO₂ + H₂). Replacing these processes with water electrolysis (2H₂O → 2H₂ + O₂) using renewable energy can significantly reduce this CO₂ emission.⁴ However, renewable electricity sources of an intermittent nature are not compatible with ammonia synthesis *via* the conventional HB process⁵ because the process is operated on large-scale and steady-state operations. On this basis, ammonia

synthesis catalysts need severe reaction conditions (at 450–600 °C and 15–40 MPa).⁵ Therefore, ammonia synthesis catalysts that work under mild conditions should be developed for ammonia synthesis using renewable electricity sources.

The rate-determining step in the synthesis of ammonia (3H₂ + N₂ → 2NH₃) is the dissociation of the N₂ triple bond (945 KJ mol⁻¹), which is the strongest bond among those in diatomic molecules.^{6,7} Supported ruthenium (Ru) catalysts are the most promising candidates for ammonia synthesis under mild conditions because optimum N₂ adsorption energy facilitates N₂ dissociation on the Ru surface.⁸ Strongly basic supports (such as CeO₂, La_{0.5}Pr_{0.5}O_{1.75}, Ba/Ce_{0.5}La_{0.5}O_{1.75}, CeO₂-PrO_x, and Ce_{0.5}La_{0.5-x}Ti_xO_{1.75+0.5x})^{9–14} further promote N₂ dissociation because the basic compounds enhance the electron transfer from the Ru metal to the antibonding orbital of N₂.¹⁵ However, hydrogen atoms generated by H₂ dissociation are often adsorbed on the active sites of the Ru surface, thereby preventing N₂ dissociation on the Ru surface.¹⁶ In recent years, oxyhydrides such as BaTiO_{3-x}H_x, BaCeO_{3-x}H_yN_z, LaH_{3-2x}O_x, GdHO, and SmHO have been reported as supports that suppress hydrogen poisoning and enhance the ammonia synthesis activity of Ru catalysts.^{17–20} Suppression of hydrogen poisoning is presumed to originate from the diffusivity of hydride (H⁻), which allows hydrogen spillover from the Ru metal to the surface of the oxyhydride supports.²¹

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ra01539d>



Transition-metal (TM) oxyhydride synthesis is generally complicated because the differences in chemical properties (such as reactivity, volatility, and ionic radius) among anions prevent different anions in an identical compound from becoming stable.²² For this reason, solid-state topochemical reactions and/or high-pressure reactions have been used to synthesize TM oxyhydrides.²² BaTiO_{3-x}H_x, which is a promising TM perovskite oxyhydride support for ammonia synthesis catalysts, cannot be prepared by simply reducing BaTiO₃ with hydrogen. However, this oxyhydride is accessible *via* a solid-state topochemical reaction involving BaTiO₃ and CaH₂ because the reaction can provide a metastable phase by exchanging the oxide (O²⁻) in BaTiO₃ with hydride (H⁻) in CaH₂ while maintaining the basic framework structure of BaTiO₃.²³ However, materials preparation using the topochemical reaction is not suitable for practical use because the reaction involves a multi-step process: (1) mixing BaTiO₃ and the moisture-sensitive CaH₂ in an inert atmosphere, (2) calcining the mixture for a week under vacuum, and (3) washing in an inert atmosphere to extract product BaTiO_{3-x}H_x by removing the residual CaH₂ and by-product CaO. The practical utility of BaTiO_{3-x}H_x may be limited by low producibility owing to the multi-step process. Thus, developing more facile, efficient ways to prepare BaTiO_{3-x}H_x is necessary to accelerate the application of BaTiO_{3-x}H_x. Moreover, the development can lead to the discovery of novel oxyhydrides.

Recently, Uchimura *et al.*²⁴ have reported the direct synthesis of BaTiO_{3-x}H_x by a mechanochemical method using BaH₂, BaO, and TiO₂ and confirmed its performance as a hydrogen-permeable electrode. However, handling in an inert atmosphere is still required because BaH₂ and BaO are sensitive to moisture. Herein, we demonstrated the synthesis of BaTiO_{3-x}H_x ($x = 0.5$), a perovskite oxyhydride, on a TiH₂ surface *via* conventional wet impregnation method using TiH₂ and Ba(OH)₂·8H₂O, which are stable in moisture and air. The obtained BaTiO_{2.5}H_{0.5} was crystallized as fine particles of 100–200 nm size that covered the TiH₂ particle surface. The Ru-loaded catalyst, Ru/BaTiO_{2.5}H_{0.5}-TiH₂, showed 2.46 times higher ammonia synthesis activity than Ru-Cs/MgO as benchmark Ru catalyst. Moreover, Ru/BaTiO_{2.5}H_{0.5}-TiH₂ suppressed hydrogen poisoning, thereby proving the formation of BaTiO_{2.5}H_{0.5} perovskite oxyhydride.

Methods

BaTiO_{2.5}H_{0.5}-TiH₂ was synthesized *via* the wet impregnation method using TiH₂ powder and Ba hydroxide solution. TiH₂ (98%, -325 mesh, Sigma-Aldrich) was impregnated with a solution containing the desired amount of Ba(OH)₂·8H₂O (98.0%, FUJIFILM Wako Chemicals) dissolved in 3 : 2 (v/v) H₂O/ethanol at 230 °C in the air, after which it was heated at 350 °C for 3 h in a 10% H₂/N₂ atmosphere. The Ba addition amounts were varied from 0–15 wt% on a Ba(OH)₂ basis. The obtained compounds are hereafter referred to as Ba(α)-TiH₂ (α : wt% of Ba(OH)₂). Reference compounds Ba(α)-TiO₂ (where α = wt% of Ba(OH)₂) were prepared using the same protocols as for Ba(α)-TiH₂, except TiO₂ (99.9%, Rutile, Sigma-Aldrich) was used

instead of TiH₂. Ba(10)-TiH₂ synthesized using Ba(CH₃COO)₂ (99.0%, FUJIFILM Wako Chemicals) or Ba(NO₃)₂ (99.0%, FUJIFILM Wako Chemicals) instead of Ba(OH)₂·8H₂O were also prepared to investigate the effect of Ba sources. Cs/MgO as a benchmark compound was prepared by impregnation using MgO (99%, Sigma-Aldrich) and Cs₂CO₃ (99.9%, Sigma-Aldrich)/ethanol solution, followed by thermal treatment at 350 °C for 3 h under 10% H₂/N₂. Ru-loaded catalysts, such as Ru/Ba(α)-TiH₂, Ru/Ba(α)-TiO₂, and Ru-Cs/MgO, were prepared by impregnation using Ru₃(CO)₁₂ (99%, Sigma-Aldrich)/tetrahydrofuran solution. The suspension was stirred for 5 h, and the solvent was subsequently evaporated at 27 °C. The obtained compound was dried at 80 °C for 16 h in the air. The Cs and Ru loading amounts were 1 wt% on a metal basis.

X-ray diffraction (XRD) patterns were collected at room temperature using SmartLab (Rigaku) with Cu K α radiation ($\lambda = 1.54056$ Å). The obtained XRD patterns were analyzed using the JANA2006 software.²⁵ The neutron diffraction (ND) pattern was collected at room temperature using the NOVA time-of-flight (TOF) neutron diffractometer at the J-PARC facility in Japan. The obtained ND pattern was analyzed using Z-Rietveld software.²⁶ Fourier-transform infrared (FT-IR) spectra were recorded using an iS50 spectrometer (Thermo Fisher) equipped with a diffuse reflectance optics accessory. Samples were pretreated at 200 °C for 30 min in flowing He and then examined at 50 °C. Scanning electron microscopy (SEM) images were obtained using a JSM-7400F (JEOL) and a SU3500 (Hitachi) operated at 1.5 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) mapping images were obtained using a Tecnai Osiris (FEI) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted on a Quantera SXM instrument (ULVAC PHI) using Al K α radiation (1486.6 eV). CO amounts adsorbed by the catalyst were estimated using a BEL-METAL-3 (MicrotracBEL). CO pulse injections (1.99% CO/He) to the samples were conducted at 50 °C after the pretreatment at 400 °C for 2 h in 100% H₂.

The ammonia synthesis activities under ambient pressure were estimated using a fixed-bed reactor connected to mass flow controllers. A sample (0.2 g) was suspended on a bed of quartz wool in a quartz tube and preheated at 400 °C for 2 h in 75% H₂/N₂ (H₂/N₂ = 3) at a flow rate of 80 mL min⁻¹. The activity measures were conducted at 300–400 °C in 75% H₂/N₂ (H₂/N₂ = 3) at a flow rate of 80 mL min⁻¹. The ammonia concentrations in the outlet of the quartz tube were monitored by FT-IR spectroscopy and converted into ammonia synthesis rates. Reaction orders of ammonia synthesis with respect to H₂, N₂, and NH₃ were estimated using the method of Aika *et al.*²⁷

Results and discussion

The XRD patterns of Ba(α)-TiH₂ ($\alpha = 0, 1, 3, 5, 10, \text{ and } 15$) predominantly showed the cubic phase of the fluorite structure ($Fm\bar{3}m$) with the lattice parameter of $a = 4.4489\text{--}4.4519$ Å (Fig. 1). The lattice parameter matches that of the reported TiH₂ ($a = 4.4512(1)$ Å),²⁸ showing that the cubic phase is TiH₂. The XRD patterns of samples with $\alpha = 0$ and 1 only showed the



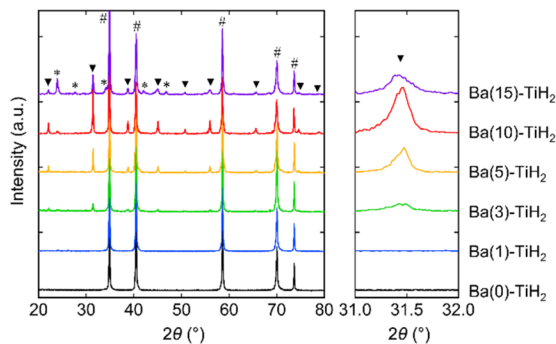


Fig. 1 XRD patterns of Ba(α)-TiH₂ ($\alpha = 0, 1, 3, 5, 10, \text{ and } 15$). Hashtags (#), triangles (▼), and asterisks (*) indicate peaks arising from TiH₂, BaTiO_{2.5}H_{0.5}, and BaCO₃, respectively.

single phase of TiH₂, whereas the XRD patterns of $\alpha \geq 3$ samples contained an additional cubic phase of perovskite structure ($Pm\bar{3}m$; Fig. S1 in the ESI†). The lattice volume was estimated to be $V = 64.926\text{--}65.073 \text{ \AA}^3$ (Table 1), which approaches that reported for cubic BaTiO_{2.38}H_{0.62} perovskite oxyhydride ($Pm\bar{3}m$, $V = 65.140 \text{ \AA}^3$)²³ rather than tetragonal BaTiO₃ perovskite oxide ($P4mm$, $V = 64.281 \text{ \AA}^3$)²⁹ which indicates that the additional cubic phase is BaTiO_{3-x}H_x perovskite oxyhydride. The H content x in BaTiO_{3-x}H_x ($\alpha = 3, 5, 10, \text{ and } 15$) were determined to be $x = 0.47\text{--}0.57$ based on Vegard's law (Table 1; hereafter, the obtained perovskite oxyhydride is referred to as BaTiO_{2.5}H_{0.5}). The formation of oxygen-deficient BaTiO_{3- δ} is unlikely because the lattice volume of BaTiO_{2.5}H_{0.5} ($V = 64.926\text{--}65.073 \text{ \AA}^3$) is larger than that reported for cubic BaTiO_{3- δ} perovskite oxide ($\delta = 0.25$, $Pm\bar{3}m$, $V = 64.337 \text{ \AA}^3$) where the lattice volume does not change through the formation of oxygen defects.³⁰ The formation of the BaTiO_{3- δ} (OH) _{δ} oxyhydroxide through OH⁻ incorporation is also denied because no peaks associated with OH bonds (observed at 3400 cm^{-1} in BaTiO₃ system)³¹ were observed by FT-IR spectroscopy (Fig. S2†). Moreover, the XRD patterns of the $\alpha = 10$ and 15 samples showed that BaCO₃ can potentially form through the reaction of unreacted Ba(OH)₂ with atmospheric CO₂ absorbed during impregnation. Thus, the addition of Ba into TiH₂ forms BaTiO_{2.5}H_{0.5} perovskite oxyhydride and BaCO₃.

Table 1 Physical characteristics of Ba(α)-TiH₂ ($\alpha = 0, 1, 3, 5, 10, \text{ and } 15$)

Sample	Lattice volume of BaTiO _{3-x} H _x ^a (\AA^3)	H content x ^b
Ba(0)-TiH ₂	—	—
Ba(1)-TiH ₂	—	—
Ba(3)-TiH ₂	65.002(2)	0.52
Ba(5)-TiH ₂	64.926(2)	0.47
Ba(10)-TiH ₂	65.009(2)	0.56
Ba(15)-TiH ₂	65.073(3)	0.57

^a Calculated from the lattice parameters based on the cubic perovskite structure ($Pm\bar{3}m$, $Z = 1$). ^b Determined from Vegard's law using the lattice volumes of BaTiO₃ ($V = 64.281 \text{ \AA}^3$)²⁹ and BaTiO_{2.38}H_{0.62} ($V = 65.140 \text{ \AA}^3$)²³.

The ND pattern of Ba(10)-TiH₂ was collected to investigate the presence of the hydride in BaTiO_{2.5}H_{0.5} (Fig. S3 and Table S1†). Rietveld refinement was performed by assuming that the secondary phase is a BaTiO_{3-x}H_x cubic perovskite with a $Pm\bar{3}m$ structural model, where Ba, Ti, and O/H atoms are placed at the Wyckoff position of $1a$ (0, 0, 0), $1b$ (0.5, 0.5, 0.5), and $3c$ (0, 0.5, 0.5), respectively. Cubic TiH₂ ($Fm\bar{3}m$) was added as a primary phase. Refinement converged to O and H occupancies of $g(\text{O}) = 0.886(2)$ and $g(\text{H}) = 0.114(2)$, which yields the BaTiO_{2.658(6)}H_{0.342(6)} composition and supports the notion that perovskite phase contains hydride. We note here that the difference in the neutron scattering lengths of oxygen and hydrogen (O: 5.803 fm, H: -3.741 fm)³² gives the composition BaTiO_{2.438(6)} when the refinement is performed by assuming that the secondary phase is oxygen-deficient BaTiO_{3- δ} . However, because the formation of oxygen-deficient BaTiO_{3- δ} is ruled out by considering the lattice volumes estimated by the XRD analysis, the ND results support the formation of an oxyhydride.

The degrees of BaTiO_{2.5}H_{0.5} and BaCO₃ formation were determined by Rietveld refinement of the XRD patterns of Ba(α)-TiH₂. We note here that components (less than about 1%) that are not detected in the XRD analysis are not considered. As shown in Fig. 2, the mass fraction of BaTiO_{2.5}H_{0.5} is 0% at $0 \leq \alpha \leq 1$ and higher at $3 \leq \alpha \leq 10$ (1.6% to 8.7%). However, a lower fraction was observed at $\alpha = 15$ (4.5%). The addition of Ba to TiH₂ facilitates the formation of BaTiO_{2.5}H_{0.5}, while excess Ba inhibits its formation. Thus, the optimum amount of Ba(OH)₂ needed to form BaTiO_{2.5}H_{0.5} corresponds to $\alpha = 10$. The mass fraction of the formed BaCO₃ was 0% at $0 \leq \alpha \leq 5$ but higher at $10 \leq \alpha \leq 15$ (0.7 to 4.3%), which implies that unreacted Ba(OH)₂ remains at $\alpha \geq 10$. The samples also exhibited colors that depend on the amounts of BaTiO_{2.5}H_{0.5} and BaCO₃ amounts (Fig. S4†). Ba(0)-TiH₂ and Ba(5)-TiH₂ are gray, which is typical of TiH₂, while Ba(10)-TiH₂ is dark blue, which is typical of BaTiO_{2.5}H_{0.5},²³ which also supports the notion that the BaTiO_{2.5}H_{0.5} perovskite oxyhydride had formed. Ba(15)-TiH₂ is brown, which is possibly due to mixed colors associated with TiH₂, BaTiO_{2.5}H_{0.5}, and BaCO₃.

The SEM image of Ba(0)-TiH₂ revealed that the particle size of TiH₂ ranged from several to tens of μm (Fig. S5 and S6†). Particle size was not affected by the amount of added Ba, which

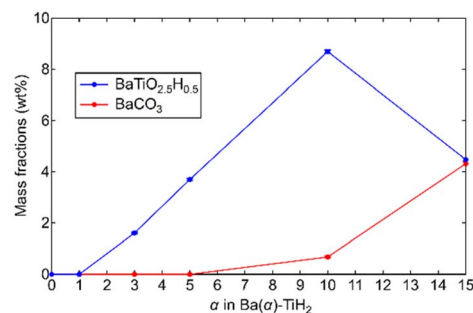


Fig. 2 Mass fractions of BaTiO_{2.5}H_{0.5} and BaCO₃ in Ba(α)-TiH₂ determined by Rietveld refinements of the XRD patterns of Ba(α)-TiH₂. Cubic TiH₂ ($Fm\bar{3}m$), cubic BaTiO_{2.5}H_{0.5} ($Pm\bar{3}m$), and orthorhombic BaCO₃ ($Pnma$) phases were applied during the analysis.



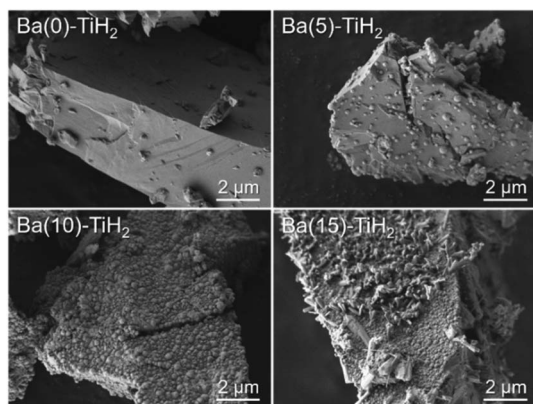


Fig. 3 SEM images of Ba(α)-TiH₂ ($\alpha = 0, 5, 10,$ and 15) at $100\ 00\times$ magnification.

agreed with the identical specific surface area of Ba(α)-TiH₂ ($0 \leq \alpha \leq 15$; $1.65\text{--}1.91\ \text{m}^2\ \text{g}^{-1}$). The particle surface of Ba(0)-TiH₂ and Ba(1)-TiH₂ were relatively smooth; by comparison, nanoparticles of *ca.* 100–200 nm were dispersed on the TiH₂ surface of Ba(3)-TiH₂ and Ba(5)-TiH₂ (Fig. 3). The nanoparticles were expected to be BaTiO_{2.5}H_{0.5} because BaTiO_{2.5}H_{0.5} in addition to TiH₂ was observed in the XRD patterns of Ba(3)-TiH₂ and Ba(5)-TiH₂ (Fig. 1). The EDX mappings in the HAADF-STEM image of Ru/Ba(5)-TiH₂ show that Ba and O elements were localized at the nanoparticles (Fig. 4), thus supporting the identification of the nanoparticles as BaTiO_{2.5}H_{0.5}. The Ba/Ti atomic ratio estimated from the XPS analysis was higher than that of the feed ratio in the preparation, also supporting that the nanoparticles are BaTiO_{2.5}H_{0.5}. The SEM image of Ba(10)-TiH₂ showed that the BaTiO_{2.5}H_{0.5} nanoparticles fully covered the TiH₂ particle. Moreover, the SEM image of Ba(15)-TiH₂ showed needle-shaped particles on the BaTiO_{2.5}H_{0.5} nanoparticles. The crystals were identified as BaCO₃ according to the XRD pattern because BaCO₃ generally formed needle-shape crystals.³³ Therefore, BaTiO_{2.5}H_{0.5} was formed as 100–200 nm nanoparticles at $\alpha \geq 3$, and BaCO₃ was formed as needle shape particles at $\alpha \geq 10$ (Fig. 5).

The XRD patterns of Ba(α)-TiO₂ ($\alpha = 0, 5, 10, 15$) synthesized as comparison are shown in Fig. S8.† All samples showed

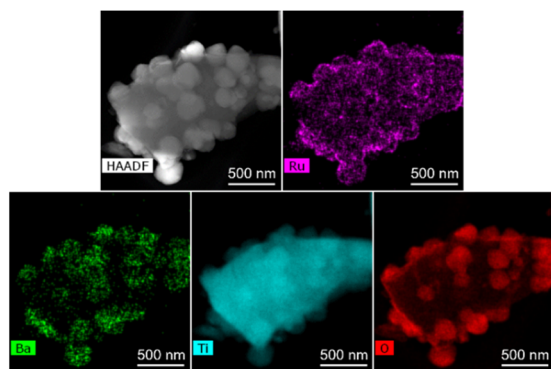


Fig. 4 STEM-HAADF and EDX mapping images of Ru/Ba(5)-TiH₂.

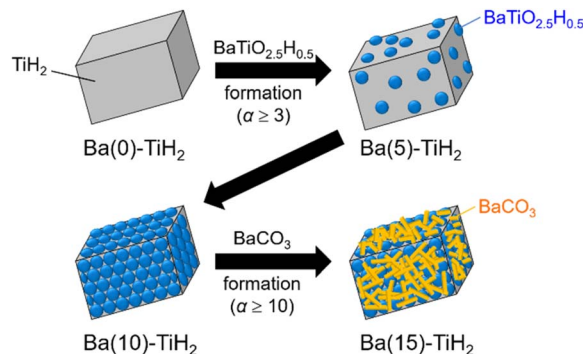


Fig. 5 Images of the morphological change of Ba(α)-TiH₂.

predominantly rutile TiO₂. Ba(0)-TiO₂ was the single phase of TiO₂, whereas Ba(α)-TiO₂ ($\alpha = 5, 10,$ and 15) contained additional Ba₂TiO₄ and BaCO₃. The cubic phase of BaTiO_{2.5}H_{0.5} formed in Ba(α)-TiH₂ was not observed with the addition of any amount of Ba(OH)₂. Therefore, TiH₂ is essential for BaTiO_{2.5}H_{0.5} formation.

How is TiH₂ involved in the formation of BaTiO_{2.5}H_{0.5}? TiH₂ consumed to form BaTiO_{2.5}H_{0.5} is calculated to be 2.1% for Ba(10)-TiH₂ which contains the highest amount of BaTiO_{2.5}H_{0.5} (8.7%; Fig. 2), suggesting that only the surface part of the TiH₂ particles contributes to the formation. This is supported by the SEM and TEM observations (Fig. 3 and 4). Because metal hydrides are generally unstable in an oxidizing atmosphere, the surface of TiH₂ particles is known to be covered by an oxide film of TiO₂.³⁴ TiH₂ (Ti²⁺) partially oxidized to TiO₂ (Ti⁴⁺) possibly contributes to the formation of BaTiO_{2.5}H_{0.5} (Ti^{3.5+}) *via* the reaction Ba(OH)₂ + 0.5xTiH₂ + (1 - 0.5x)TiO₂ → BaTiO_{3-x}H_x + H₂O. Moreover, the effect of Ba reagents on BaTiO_{2.5}H_{0.5} formation was investigated. The XRD patterns of Ba(10)-TiH₂ synthesized using Ba(CH₃COO)₂ or Ba(NO₃)₂ instead of Ba(OH)₂·8H₂O are shown in Fig. S9.† The XRD pattern of Ba(10)-TiH₂ synthesized *via* Ba(CH₃COO)₂ showed only TiH₂ and Ba(CH₃COO)₂ and no formation of BaTiO_{2.5}H_{0.5}. While Ba(10)-TiH₂ synthesized *via* Ba(NO₃)₂ contained BaTiO_{2.5}H_{0.5}, its mass fraction (1.5%) was only 0.17-times that of the Ba(10)-TiH₂ synthesized *via* Ba(OH)₂·8H₂O (8.7%). These observations suggest that the hydroxide ion (OH⁻) promotes the formation of BaTiO_{2.5}H_{0.5}.

The ammonia synthesis activities of Ru/Ba(α)-TiH₂ ($0 \leq \alpha \leq 15$) catalysts were examined at 300–400 °C under ambient pressure (Fig. 6a). Ammonia synthesis rates of all catalysts increased at elevated temperature. Ru/Ba(0)-TiH₂ exhibited ammonia synthesis activity at ≥ 375 °C. The ammonia synthesis rate of Ru/Ba(0)-TiH₂ ($0.05\ \text{mmol}\ \text{g}^{-1}\ \text{h}^{-1}$ at 400 °C) was 0.04 times that of Ru/Cs-MgO ($1.24\ \text{mmol}\ \text{g}^{-1}\ \text{h}^{-1}$ at 400 °C), which was often called as benchmark Ru catalysts.^{35,36} The activity of Ru/Ba(1)-TiH₂ ($0.20\ \text{mmol}\ \text{g}^{-1}\ \text{h}^{-1}$ at 400 °C) was higher than that of Ru/Ba(0)-TiH₂ but remained lower than that of Ru/Cs-MgO. However, by contrast, the activities of Ru/Ba(3)-TiH₂, Ru/Ba(5)-TiH₂, and Ru/Ba(10)-TiH₂ ($1.73, 2.08,$ and $3.05\ \text{mmol}\ \text{g}^{-1}\ \text{h}^{-1}$ at 400 °C, respectively) were higher than that of Ru-Cs/MgO by a factor of 1.40, 1.68, and 2.46, respectively. Activity increased



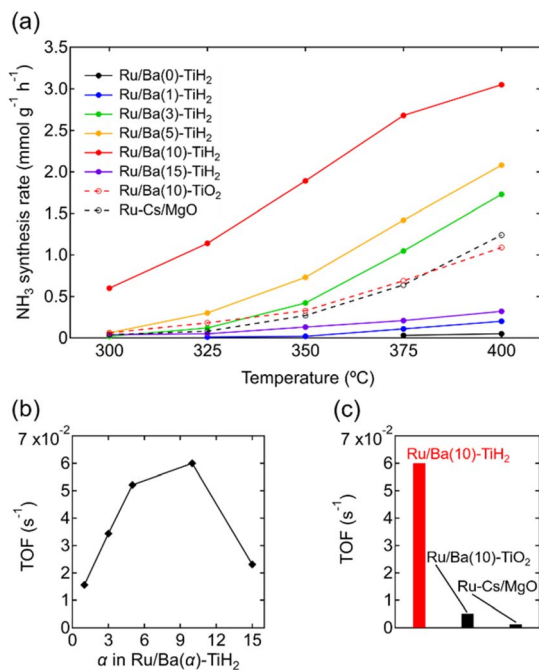


Fig. 6 (a) Temperature dependence of the NH₃ synthesis rates for Ru/Ba(α)-TiH₂ ($\alpha = 0, 1, 3, 5, 10,$ and 15), Ru/Ba(10)-TiO₂, and Ru-Cs/MgO (reaction conditions: catalyst, 0.2 g; reaction gas, H₂/N₂ = 3 at a flow rate of 80 mL min⁻¹; pressure = ambient pressure). (b) TOF of Ru/Ba(α)-TiH₂ ($\alpha = 0, 1, 3, 5, 10,$ and 15) at 350 °C as functions of Ba(OH)₂ added amount α . (c) TOF of Ru/Ba(10)-TiH₂, Ru/Ba(10)-TiO₂, and Ru-Cs/MgO at 350 °C.

with the increase in Ba addition amount in $0 \leq \alpha \leq 10$, whereas the activity decreased at $\alpha = 15$ ($0.32 \text{ mmol g}^{-1} \text{ h}^{-1}$ at 400 °C). Therefore, the most active catalyst among Ru/Ba(α)-TiH₂ ($0 \leq \alpha \leq 15$) was Ru/Ba(10)-TiH₂. The activity of Ru/Ba(10)-TiH₂ was higher than that of Ru/Ba(10)-TiO₂ ($1.09 \text{ mmol g}^{-1} \text{ h}^{-1}$ at 400 °C), thereby suggesting that BaTiO_{2.5}H_{0.5} formation was responsible for the high activity of Ru/Ba(10)-TiH₂.

The TOF for the ammonia synthesis reaction at 350 °C was estimated to obtain a deeper insight into the correlation between ammonia synthesis activity and catalyst composition. As shown in Fig. 6b, the TOF of Ru/Ba(α)-TiH₂ increased with increasing amount of Ba addition at $1 \leq \alpha \leq 10$ ($1.56 \times 10^{-2} \text{ s}^{-1}$ to $6.00 \times 10^{-2} \text{ s}^{-1}$) but decreased at $\alpha = 15$ ($2.31 \times 10^{-2} \text{ s}^{-1}$). This trend was consistent with the trend of the mass fraction of BaTiO_{2.5}H_{0.5} (Fig. 2); these observations support that BaTiO_{2.5}H_{0.5} formation contributes to the increase in ammonia synthesis activity. This was supported by the fact that the TOF of Ru/Ba(10)-TiH₂ ($6.00 \times 10^{-2} \text{ s}^{-1}$) was 12 and 46 times larger than those of Ru/Ba(10)-TiO₂ ($0.51 \times 10^{-2} \text{ s}^{-1}$) and Ru-Cs/MgO ($0.13 \times 10^{-2} \text{ s}^{-1}$), respectively (Fig. 6c). Interestingly, the TOF of Ru/Ba(15)-TiH₂ ($2.31 \times 10^{-2} \text{ s}^{-1}$) was lower than that of Ru/Ba(5)-TiH₂ ($5.21 \times 10^{-2} \text{ s}^{-1}$) despite the higher mass fraction of BaTiO_{2.5}H_{0.5} for Ru/Ba(15)-TiH₂ (4.48%) than that for Ru/Ba(5)-TiH₂ (3.70%). The formation of BaCO₃, which partially covered the BaTiO_{2.5}H_{0.5} particles (Fig. 3), was expected to inhibit the ammonia synthesis reaction of Ru/Ba(15)-TiH₂ because BaCO₃ was stable in the reaction temperature.³⁷

Table 2 Reaction orders^a for ammonia synthesis reaction over Ru/Ba(10)-TiH₂ and Ru-Cs/MgO

Catalyst	Order		
	H ₂	N ₂	NH ₃
Ru/Ba(10)-TiH ₂	0.15	0.79	-0.36
Ru-Cs/MgO	-0.59	0.89	0.11

^a Estimated from results of kinetic analysis shown in Fig. S8.

Finally, reaction orders with respect to H₂, N₂ and NH₃ were investigated using the method of Aika *et al.*²⁷ (Fig. S10 and Table S3†). The H₂ order of Ru/Ba(10)-TiH₂ (0.15) was higher than that of Ru-Cs/MgO (-0.59), reflecting that compared to Ru-Cs/MgO, Ru/Ba(10)-TiH₂ had less hydrogen poisoning, which prevented N₂ dissociation on Ru (Table 2).¹⁶ The low hydrogen poisoning effect allowed Ru/Ba(10)-TiH₂ to exhibit higher ammonia synthesis activity than Ru-Cs/MgO. The N₂ orders of Ru/Ba(10)-TiH₂ (0.79) and Ru-Cs/MgO (0.89) were virtually coincident, reflecting that the rate-determining step for both catalysts was the unimolecular cleavage reaction of N₂ for both catalysts. Moreover, the orders of Ru/Ba(10)-TiH₂ (H₂ order: 0.15, N₂ order: 0.79) agreed well with the reported orders of Ru/BaTiO_{2.5}H_{0.5} (H₂ order: 0.2, N₂ order: 0.7).¹⁷ Because Ru/BaTiO₃, the reference catalyst for Ru/BaTiO_{2.5}H_{0.5}, exhibits stronger hydrogen poisoning due to the absence of hydride in the support perovskite (H₂ order: -0.89, N₂ order: 1.2),¹⁷ the agreement of the H₂ and N₂ orders between Ru/Ba(10)-TiH₂ and Ru/BaTiO_{2.5}H_{0.5} supports the formation of BaTiO_{2.5}H_{0.5} in Ru/Ba(10)-TiH₂. The NH₃ order of Ru/Ba(10)-TiH₂ (-0.36) was higher than that reported for Ru/BaTiO_{2.5}H_{0.5} (-0.64), indicating that the ammonia decomposition reaction on Ru/Ba(10)-TiH₂ was relatively inhibited. The inhibition may be attributed to the reaction pressure of this study (ambient pressure) being lower than that of reported Ru/BaTiO_{2.5}H_{0.5} (5 MPa) because the ammonia decomposition reaction generally proceeded at a higher pressure.³⁸

Conclusions

The selection of appropriate raw materials allowed for BaTiO_{2.5}H_{0.5} perovskite oxyhydride nanoparticles to be formed on the TiH₂ surface through the conventional wet impregnation method. BaTiO_{2.5}H_{0.5} crystallized as *ca.* 100–200 nm sized nanoparticles on the surface of TiH₂. Hydroxide in Ba(OH)₂ involved BaTiO_{2.5}H_{0.5} formation. Ru-loaded catalysts inhibited hydrogen poisoning and showed higher ammonia synthesis activity compared to that of the Ru-Cs/MgO benchmark catalyst. We believe that further investigation of oxyhydride prepared *via* the wet impregnation method accelerates the use of oxyhydride as ammonia synthesis catalysts.

Author contributions

Yoshihiro Goto: conceptualization, investigation, writing – original draft, Masashi Kikugawa: investigation, Keisuke



Kobayashi: data curation, Yuichi Manaka: validation, Tetsuya Nanba: conceptualization, project administration, Hideyuki Matsumoto: formal analysis Mitsuru Matsumoto: validation, Masakazu Aoki: supervision, project administration, Haruo Imagawa: supervision, writing-review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge Mr Akira Takatsuki (National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan) for his contribution in collecting the SEM and STEM-HAADF images.

Notes and references

- J. W. Erisman, M. A. Sutton, J. Galloway, Z. Klimont and W. Winiwarter, *Nat. Geosci.*, 2008, **1**, 636.
- A. Klerke, C. H. Christensen, J. K. Nørskov and T. Vegge, *J. Mater. Chem.*, 2008, **18**, 2304.
- P. H. Pfromm, *J. Renewable Sustainable Energy*, 2017, **9**, 034702.
- C. Smith, A. K. Hill and L. Torrente-Murciano, *Energy Environ. Sci.*, 2020, **13**, 331.
- M. Ravi and J. W. Makepeace, *Chem. Sci.*, 2022, **13**, 890.
- S. Gambarotta and J. Scott, *Angew. Chem., Int. Ed.*, 2004, **43**, 5298.
- K. Honkala, A. Hellman, I. N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C. H. Christensen and J. K. Nørskov, *Science*, 2005, **307**, 555.
- C. J. H. Jacobsen, S. Dahl, B. S. Clausen, S. Bahn, A. Logadottir and J. K. Nørskov, *J. Am. Chem. Soc.*, 2001, **123**, 8404.
- Y. Niwa and K. Aika, *Chem. Lett.*, 1996, **3**, 3.
- Y. Ogura, K. Tsujimaru, K. Sato, S. Miyahara, T. Toriyama, T. Yamamoto, S. Matsumura and K. Nagaoka, *ACS Sustainable Chem. Eng.*, 2018, **6**, 17258.
- Y. Ogura, K. Sato, S. Miyahara, Y. Kawano, T. Toriyama, T. Yamamoto, S. Matsumura, S. Hosokawa and K. Nagaoka, *Chem. Sci.*, 2018, **9**, 2230.
- K. Sato, S. Miyahara, Y. Ogura, K. Tsujimaru, Y. Wada, T. Toriyama, T. Yamamoto, S. Matsumura and K. Nagaoka, *ACS Sustainable Chem. Eng.*, 2020, **8**, 2726.
- M. Kikugawa, Y. Goto, K. Kobayashi, T. Nanba, H. Matsumoto and H. Imagawa, *J. Catal.*, 2022, **413**, 934.
- Y. Goto, M. Kikugawa, K. Kobayashi, T. Nanba, H. Matsumoto and H. Imagawa, *Chem. Commun.*, 2022, **58**, 3210.
- K. Aika, A. Ohya, A. Ozaki, Y. Inoue and I. Yasumori, *J. Catal.*, 1985, **92**, 305.
- Y. Kadowaki and K. Aika, *J. Catal.*, 1996, **161**, 178.
- Y. Tang, Y. Kobayashi, N. Masuda, Y. Uchida, H. Okamoto, T. Kageyama, S. Hosokawa, F. Loyer, K. Mitsuhara, K. Yamanaka, Y. Tamenori, C. Tassel, T. Yamamoto, T. Tanaka and H. Kageyama, *Adv. Energy Mater.*, 2018, **8**, 1801772.
- M. Kitano, J. Kujirai, K. Ogasawara, S. Matsuishi, T. Tada, H. Abe, Y. Niwa and H. Hosono, *J. Am. Chem. Soc.*, 2019, **141**, 20344.
- K. Ooya, J. Li, K. Fukui, S. Iimura, T. Nakao, K. Ogasawara, M. Sasase, H. Abe, Y. Niwa, M. Kitano and H. Hosono, *Adv. Energy Mater.*, 2021, **11**, 2003723.
- H. Yamashita, T. Broux, Y. Kobayashi, F. Takeiri, H. Ubukata, T. Zhu, M. A. Hayward, K. Fujii, M. Yashima, K. Shitara, A. Kuwabara, T. Murakami and H. Kageyama, *J. Am. Chem. Soc.*, 2018, **140**, 11170.
- K. Wang, Z. Wu and D. Jiang, *Phys. Chem. Chem. Phys.*, 2022, **24**, 1496.
- H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli and K. R. Poeppelmeier, *Nat. Commun.*, 2018, **9**, 772.
- Y. Kobayashi, O. J. Hernandez, T. Sakaguchi, T. Yajima, T. Roisnel, Y. Tsujimoto, M. Morita, Y. Noda, Y. Mogami, A. Kitada, M. Ohkura, S. Hosokawa, Z. Li, K. Hayashi, Y. Kusano, J. E. Kim, N. Tsuji, A. Fujiwara, Y. Matsushita, K. Yoshimura, K. Takegoshi, M. Inoue, M. Takano and H. Kageyama, *Nat. Mater.*, 2012, **11**, 507.
- T. Uchimura, F. Takeiri, K. Okamoto, T. Saito, T. Kamiyama and G. Kobayashi, *J. Mater. Chem. A*, 2021, **9**, 20371.
- V. Petříček, M. Dušek and L. Palatinus, *Z. Kristallogr. Cryst. Mater.*, 2004, **229**, 345.
- R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama, *Nucl. Instrum. Methods Phys. Res. A: Accel. Spectrom. Detect. Assoc. Equip.*, 2009, **600**, 94.
- K. Aika, M. Kumasaka, T. Oma, O. Kato, H. Matsuda, N. Watanabe, K. Yamazaki, A. Ozaki and T. Onishi, *Appl. Catal.*, 1986, **28**, 57.
- P. E. Kalita, S. V. Sinogeikin, K. E. Lipinska-Kalita, T. Hartmann, X. Ke, C. Chen and A. L. Cornelius, *J. Appl. Phys.*, 2010, **108**, 043511.
- R. H. Buttner and E. N. Maslen, *Acta Crystallogr.*, 1992, **B48**, 764.
- I.-K. Jeong, S. Lee, S. Jeong, C. J. Won, N. Hur and A. Llobet, *Phys. Rev. B*, 2011, **84**, 064125.
- P. R. Arya, P. Jha and A. K. Ganguli, *J. Mater. Chem.*, 2003, **13**, 415.
- V. F. Sears, *Neutron News*, 1992, **2**, 26.
- B. Sreedhar, Ch. Satya Vani, D. Keerthi Devi, V. Sreeram and M. V. Basaveswara Rao, *Am. J. Mater. Sci.*, 2012, **2**, 105.
- K. B. Park, J. H. Choi, T. W. Na, J. W. Kang, K. S. Park and H. K. Park, *Metals*, 2019, **9**, 1154.
- K. Aika, H. Hori and A. Ozaki, *J. Catal.*, 1972, **27**, 424.
- F. Rosowski, A. Hornung, O. Hinrichsen, D. Herein, M. Muhler and G. Ertl, *Appl. Catal., A*, 1997, **151**, 443.
- X. Zhang, Q. Ye, B. Xu and D. He, *Catal. Lett.*, 2007, **117**, 140.
- F. Hayashi, Y. Toda, Y. Kanie, M. Kitano, Y. Inoue, T. Yokoyama, M. Hara and H. Hosono, *Chem. Sci.*, 2013, **4**, 3124.

