Carbon-free H₂ production from ammonia triggered at room temperature with an acidic RuO₂/γ-Al₂O₃ catalyst

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Ammonia has been suggested as a carbon-free hydrogen source, but a convenient method for producing hydrogen from ammonia with rapid initiation has not been developed. Ideally, this method would require no external energy input. We demonstrate hydrogen production by exposing ammonia and O₂ at room temperature to an acidic RuO₂/γ-Al₂O₃ catalyst. Because adsorption of ammonia onto the catalyst is exothermic, the catalyst bed is rapidly heated to the catalytic ammonia autoignition temperature, and subsequent oxidative decomposition of ammonia produces hydrogen. A differential calorimeter combined with a volumetric gas adsorption analyzer revealed a large quantity of heat evolved both with chemisorption of ammonia onto RuO₂ and acidic sites on the γ-Al₂O₃ and with physisorption of multiple ammonia molecules.

INTRODUCTION

Hydrogen has received considerable attention as a clean energy source because the only product of its reaction with oxygen is water, and very high energy conversion efficiency is obtained when it is combined with fuel cell technologies (1–4). However, low energy density by volume and handling difficulties are drawbacks for the commercial application of hydrogen gas. These problems could be overcome by using hydrogen carriers, such as methanol (5, 6), formic acid (7, 8), and ammonia borane (9, 10). Among these carriers, ammonia is a promising candidate because of its low production cost, high energy density (12.8 GJ m⁻³), and ease of liquefaction at room temperature (11–21). A carbon-free hydrogen storage and transportation system based on ammonia as a hydrogen carrier could be used to realize a carbon-free society (13, 14, 16, 17, 19, 20). When hydrogen is produced by catalytic ammonia decomposition (Eq. 1), a trace amount of ammonia is included in the hydrogen stream. Although traces of ammonia in the hydrogen stream sharply degrade the performance of the most commonly used polymer electrolyte fuel cells (22, 23), alkaline fuel cells that are not affected by relatively high volume fractions of ammonia (up to 9%) have been reported (24). Recently, anion exchange membranes have been developed as alternatives to the conventional potassium hydroxide electrolyte; these membranes have increased the potential and importance of alkaline fuel cells using hydrogen produced from ammonia (20). Although igniting pure ammonia on its own is difficult, a mixture containing as little as 10% hydrogen produced from ammonia can be readily combusted in an engine or turbine (25). Currently, there is an active national project in Japan to create a low-carbon and hydrogen-based society using ammonia as a hydrogen carrier (26).

As mentioned, hydrogen produced from ammonia is used in fuel cells, engines, and turbines. However, adoption of ammonia as a hydrogen source, especially for transportable devices and automobiles, has been limited, largely because of the absence of an efficient process for decomposing ammonia to hydrogen and nitrogen (16–18, 27). Overcoming this issue will require the development of a process with rapid initiation and a high rate of hydrogen formation but without the need for external energy input (27). Conventionally, hydrogen is produced by catalytic decomposition of ammonia (Eq. 1). Ammonia decomposition catalysts have been reviewed by Yin et al. (28) and Schüth et al. (13). Among the available metal catalysts, such as Ru, Ir, Ni, and Fe, supported Ru catalysts are highly active. On the other hand, a new class of ammonia decomposition catalysts, such as sodium amide (17) and nonstoichiometric lithium imide (18), also show high activity. Despite their availability, using these highly active catalysts remains challenging because the endothermic nature of ammonia decomposition requires that the catalyst be continuously heated by an external heat source during the reaction. Typically, a high temperature is needed for ammonia decomposition; for example, equilibrium calculations show that a temperature of 400°C is required to convert 99.1% of ammonia to its decomposition products at 0.1 MPa. Heating the catalyst from room temperature to the required reaction temperature using an external heat source takes time and energy.

\[
\text{NH}_3(g) \rightarrow 1.5\text{H}_2(g) + 0.5\text{N}_2(g) \\
\Delta H = +45.9 \text{ kJ mol}^{-1}
\]

(1)

\[
\text{NH}_3(g) + 0.25\text{O}_2(g) \rightarrow \text{H}_2(g) + 0.5\text{N}_2(g) + 0.5\text{H}_2\text{O}(g) \\
\Delta H = -75 \text{ kJ mol}^{-1}
\]

(2)

\[
\text{NH}_3(g) + 0.75\text{O}_2(g) \rightarrow 0.5\text{N}_2(g) + 1.5\text{H}_2\text{O}(g) \\
\Delta H = -317 \text{ kJ mol}^{-1}
\]

(3)

Here, we present an innovative process for the production of hydrogen from ammonia without the need for an external heat source to initiate or maintain the reaction. In this reaction, immediately after exposure of ammonia and O₂ to a pretreated catalyst consisting of RuO₂ nanoparticles supported on γ-Al₂O₃ at room temperature (~25°C), exothermic oxidative decomposition of ammonia (Eq. 2) is triggered, and hydrogen is produced at a high rate. Before use, the RuO₂/γ-Al₂O₃ catalyst is treated under an inert gas (that is, He) at 300°C to remove H₂O and CO₂ adsorbed on the catalyst, resulting in the formation of ammonia adsorption sites, such as Lewis acid sites (Fig. 1). Upon addition of a gas mixture
containing ammonia and O₂ to the catalyst at room temperature, ammonia is adsorbed onto the catalyst, thereby generating substantial heat. This heat rapidly increases the catalyst bed temperature to the catalytic autoignition temperature of ammonia combustion (Eq. 3), and oxidative decomposition of ammonia begins. Because the temperature of the catalyst bed during the reaction is higher than 300°C, the adsorbed ammonia is desorbed in situ (self-regeneration of NH₃ adsorption sites). If the catalyst is cooled without exposure to ammonia, then the ammonia adsorption sites remain unoccupied. In subsequent cycles, to reboot the process, the oxidative decomposition of ammonia can be repeatedly triggered from room temperature without heat treatment in an inert gas. This completes a catalytic cycle that requires no external energy source. Furthermore, oxidative decomposition (Eq. 2) is a combination of exothermic combustion (Eq. 3) and subsequent endothermic decomposition (Eq. 1). In this reaction, the heat produced by ammonia combustion is used for ammonia decomposition. Because of these exothermic and endothermic features, oxidative decomposition of ammonia produces hydrogen at a higher rate than conventional ammonia decomposition. Note that equilibrium calculation (fig. S1) shows that O₂ is thermodynamically consumed from 25° to 1000°C and that NH₃ conversion reaches >99% above 350°C. The maximum H₂ yield is 67%, and the 33% of hydrogen atoms remaining in ammonia are converted to water vapor. Depending on the system in which the process is applied, the produced water vapor may be removed. For example, when the process is applied to fuel cells working at low temperatures, part of the water vapor is liquefied and removed automatically before the produced gas mixture is fed to the fuel cell stack. For application in engines and turbines, removal of water is basically unnecessary, but some of the water vapor may be removed to increase the concentration of H₂.

We have reported that the heat produced by the oxidation of reduced supported metal catalysts, such as Rh/CeO₂₋ₓ and Rh/ Ce₀.₅Zr₀.₅O₂₋ₓ, can be used to trigger oxidative reforming of hydrocarbons (29–32). In this process, a typical exothermic reaction (that is, oxidation of a substance) is used for heating the catalysts, which means that reduction of the catalyst using hydrogen is required. Leakage of air into the reactor during the shutdown period must be strictly avoided because it can lead to oxidation of the catalyst and decrease the heat produced by the oxidation. In this case, the process can no longer be rebooted. In contrast, we developed here a new approach in which the heat generated by molecular adsorption (that is, the heat of ammonia adsorption) is used to heat the catalyst.

RESULTS

Triggering tests for ammonia oxidative decomposition at room temperature

The catalyst bed temperature and the formation rates of hydrogen and nitrogen at the exit of the reactor were measured during a triggering test over the RuO₂/γ-Al₂O₃ catalyst (Fig. 2, A and B). X-ray diffraction, x-ray photoelectron spectroscopy, and high-angle annular dark-field scanning transmission electron micrograph (HAADF-STEM) measurements revealed that the RuO₂ nanoparticles (1.5 ± 0.4 nm) were supported on γ-Al₂O₃ (fig. S2). The catalyst was pretreated in He at 300°C and then cooled to room temperature (fig. S3). The feed gas, with a 4:1 molar ratio of NH₃ to O₂ (equivalent to that for the ammonia oxidative decomposition shown in Eq. 2, was supplied to the catalyst. The tests were performed under quasi-adiabatic conditions (fig. S4) without external heating of the catalyst, which means that the power to the furnace was switched off during the measurements. Initially (10 s), N₂ was the only gaseous product. However, by 15 s, the formation rate of hydrogen markedly increased to 14 liters hour⁻¹ gcat⁻¹ (gcat gram of catalyst). This increase continued up to 20 s, at which point the hydrogen formation rate exceeded that of N₂, and a sharp increase in the temperature at the inlet of the catalyst bed to 522°C was observed. These results indicate that combustion and subsequent oxidative decomposition of ammonia were initiated sequentially. At 300 s, we observed the temperature distribution of the catalyst bed (Fig. 2C) using a two-color radiometric thermal imaging system (fig. S5). The temperature of the inlet was higher than that of the outlet of the catalyst bed during the reaction, which indicates that combustion (Eq. 3) and subsequent decomposition (Eq. 1) of ammonia occurred in the catalyst bed.

The formation rate of each gas approached stable values at 300 s, indicating that the heat, including external heat losses, was nearly balanced between the exothermic and endothermic reactions. Gas
analysis after 30 min of reaction revealed complete consumption of O₂. At this time, an ammonia conversion rate of 96% and a hydrogen yield of 64% were obtained. This hydrogen yield is close to the maximum value (67%) calculated, assuming a stoichiometric reaction between ammonia and O₂ (Eq. 2). The achieved hydrogen formation rate was 43 liters hour⁻¹ g⁻¹ cat⁻¹. In addition, a low concentration of ammonia was detected passing through the reactor in the mass spectrometry analysis at the beginning of the reaction (fig. S6A). However, NO, NO₂, and N₂O were not observed during the activity test (fig. S6A). In this process, NOₓ species may be produced as intermediates. Nevertheless, these species should eventually be reduced to N₂ because the Ru catalyst reduces NOₓ in the presence of hydrogen (33, 34). These results (fig. 2 and fig. S6A) reveal that oxidative decomposition of ammonia was rapidly triggered over pretreated RuO₂/γ-Al₂O₃ without any external heat input.

Next, we investigated the influence of the gas hourly space velocity (GHSV) by varying the flow rate of the gas mixture (from 104.2 to 402.7 ml min⁻¹) over a constant weight of the catalyst. For all cases, hydrogen was produced immediately, and oxidative decomposition of ammonia was triggered (fig. S7). As the GHSV increased from 31.2 to 120.8 liters hour⁻¹ g⁻¹ cat⁻¹, the initial H₂ and N₂ formation rates and the initial temperature at the inlet of the catalyst bed increased (fig. S7), and the high-temperature region of the catalyst bed at 300 s broadened (fig. S8). In addition, NH₃ conversion and H₂ yield after 30 min increased with increasing GHSV (table S1). Apparently, heat produced by ammonia combustion (Eq. 3) increased with increasing flow rate; thus, the temperature of the catalyst increased, and this heat was effectively used for endothermic ammonia decomposition (Eq. 1).

We then changed the NH₃ to O₂ molar ratio in the feed gas from 4:1 to 4:1.5 (Eq. 4) and 4:0.38 (Eq. 5).

\[
\text{NH}_3(g) + 0.37\text{O}_2(g) \rightarrow 0.76\text{H}_2(g) + 0.5\text{N}_2(g) + 0.74\text{H}_2\text{O}(g)
\]
\[
\Delta H = -135 \text{kJ mol}^{-1}
\]

\[
\text{NH}_3(g) + 0.09\text{O}_2(g) \rightarrow 1.32\text{H}_2(g) + 0.5\text{N}_2(g) + 0.18\text{H}_2\text{O}(g)
\]
\[
\Delta H = 0 \text{kJ mol}^{-1}
\]

For all tested conditions, oxidative decomposition of ammonia was triggered successfully (table S2), suggesting that the operating conditions...
of this process can be adjusted as required for the heat demand and mass integration of the total system. Notably, oxidative decomposition of ammonia was not triggered at room temperature with RuO$_2$/γ-Al$_2$O$_3$ pretreated in He at 250°C or with RuO$_2$/La$_2$O$_3$, which is an active ammonia decomposition catalyst (35), when pretreated in He at 250°C to 700°C. Neither combustion nor decomposition of ammonia occurred over these catalysts, implying that the heat produced by ammonia adsorption was insufficient to heat these catalysts to the autoignition temperature, as revealed below.

Characterization of the catalysts
To elucidate the cause of the differences in behavior observed between the RuO$_2$/γ-Al$_2$O$_3$ and RuO$_2$/La$_2$O$_3$ catalysts pretreated at 300°C during the triggering tests, we compared the maximum catalyst bed temperatures achieved with self-heating induced through ammonia adsorption. For this purpose, NH$_3$/He was supplied to the catalysts at room temperature after He pretreatment at 300°C. The catalyst bed temperature of RuO$_2$/γ-Al$_2$O$_3$ had increased to 97°C after 4 s (Fig. 3). By comparison, the maximum catalyst bed temperature of the RuO$_2$/La$_2$O$_3$ catalyst was 44°C lower (53°C). The support material, γ-Al$_2$O$_3$, is known to have acidic sites, whereas La$_2$O$_3$ is basic. Therefore, we assumed that basic ammonia was easily adsorbed onto γ-Al$_2$O$_3$, resulting in the evolution of substantial heat for heating the RuO$_2$/γ-Al$_2$O$_3$ catalyst.

We performed ammonia temperature-programmed desorption measurements (NH$_3$ TPD) to study ammonia adsorption behavior on the catalysts. Ammonia desorption over RuO$_2$/γ-Al$_2$O$_3$ was less than that over bare γ-Al$_2$O$_3$ (see fig. S9). However, in the NH$_3$ TPD profile of RuO$_2$/γ-Al$_2$O$_3$, N$_2$ formation and H$_2$O formation were observed from about 90°C and 100°C, respectively. These results indicate that NH$_3$ reacted with O$^\circ$ of RuO$_2$ and that N$_2$ and H$_2$O were formed from those temperatures; thus, it is not possible to measure the amount of ammonia adsorbed on the catalyst by using this method. Therefore, we moved on to using a differential calorimeter combined with a volumetric gas adsorption analyzer.

Calorimetry revealed much stronger heat evolution over RuO$_2$/γ-Al$_2$O$_3$ (that is, –88 J g$_{\text{cat}}^{-1}$ with an adsorption-equilibrium pressure of 72 kPa) than over RuO$_2$/La$_2$O$_3$ (that is, –9.2 J g$_{\text{cat}}^{-1}$ with an adsorption-equilibrium pressure of 72 kPa) (Fig. 4A). Notably, the partial pressure of ammonia in the triggering tests was 72 kPa. At the adsorption-equilibrium pressure, the total amount of ammonia adsorbed for RuO$_2$/γ-Al$_2$O$_3$ (1.4 mmol g$_{\text{cat}}^{-1}$) was 88 times that for RuO$_2$/La$_2$O$_3$ (0.16 mmol g$_{\text{cat}}^{-1}$).

In addition, heat evolution over bare γ-Al$_2$O$_3$ at 72 kPa was –67 J g$_{\text{cat}}^{-1}$ and only 76% of that over RuO$_2$/γ-Al$_2$O$_3$ (–88 J g$_{\text{cat}}^{-1}$). Under the same conditions, the total amount of adsorbed ammonia for bare γ-Al$_2$O$_3$ (1.3 mmol g$_{\text{cat}}^{-1}$) was only 90% of that for RuO$_2$/γ-Al$_2$O$_3$ (1.4 mmol g$_{\text{cat}}^{-1}$). These results indicate that the surfaces of the RuO$_2$ nanoparticles also acted as strong ammonia adsorption sites. Furthermore, the differential heat of ammonia adsorption for RuO$_2$/γ-Al$_2$O$_3$ and bare γ-Al$_2$O$_3$ decreased gradually with an increase in the total amount of ammonia adsorbed (Fig. 4B) and approached a stable value. These results indicate that both physisorbed and chemisorbed ammonia contributed to the heat evolution of the catalyst. The CO chemisorption capacities were measured to compare the number of surface ruthenium atoms after exposure to mild reduction conditions. The amount of CO chemisorbed on RuO$_2$/γ-Al$_2$O$_3$ was much larger than that on RuO$_2$/La$_2$O$_3$, indicating formation of fine and large RuO$_2$ particles on γ-Al$_2$O$_3$ (see fig. S2C for the HAADF-STEM image) and La$_2$O$_3$, respectively (table S3). Because γ-Al$_2$O$_3$ has a high specific surface area, fine RuO$_2$ nanoparticles, which have a high ratio of ammonia adsorption sites per mass, can be formed and many Lewis acid sites can be created during pretreatment under He at 300°C. Therefore, we conclude that a large amount of ammonia is chemisorbed onto RuO$_2$ and γ-Al$_2$O$_3$, which further increases the amount of multilayer physisorbed ammonia (Fig. 4C). This ammonia adsorption on RuO$_2$/γ-Al$_2$O$_3$ causes strong heat evolution that enables the triggering of oxidative decomposition of ammonia. In contrast, we attribute the weak heat evolution over RuO$_2$/La$_2$O$_3$ to the adsorption of ammonia onto large RuO$_2$ nanoparticles, which have a lower ratio of ammonia adsorption sites per mass, and consequently, less physisorption occurs.

To start an oxidation reaction, such as ammonia combustion (Eq. 3), the catalyst must be heated to a minimum temperature, called the catalytic autoignition temperature, at which point the reaction can proceed at a rate that produces more heat than is removed from the system by convection from the gas flow (29). After the ammonia combustion is ignited, the exothermic oxidative decomposition of ammonia quickly reaches the operation point, which is given by the sum of the heat flux produced by exothermic ammonia combustion and endothermic ammonia decomposition and by the removal of heat through convection and transmission through the wall of the reactor. We measured and compared the catalytic autoignition temperatures of RuO$_2$/γ-Al$_2$O$_3$ and RuO$_2$/La$_2$O$_3$ catalysts. After He pretreatment at 300°C, an NH$_3$/He mixture was supplied to RuO$_2$/γ-Al$_2$O$_3$ for 10 min at 80°C, and O$_2$ was then added to the reactant mixture. The catalyst bed temperature increased slightly (Fig. 5A) and then decreased to the original temperature (80°C). In contrast, upon addition of O$_2$ to the NH$_3$/He mixture at 90°C, the catalyst bed temperature of the RuO$_2$/γ-Al$_2$O$_3$ catalyst increased sharply after 15 s, indicating that ammonia combustion was ignited at 90°C. Thus, the catalytic autoignition temperature of RuO$_2$/γ-Al$_2$O$_3$ was determined to be 90°C, which is lower than the maximum catalyst bed temperature (97°C) achieved by exposing the catalyst to NH$_3$/He gas at room temperature (Fig. 3). Also note that 90°C is nearly identical to the temperature at which N$_2$ and H$_2$O were observed during NH$_3$ TPD measurements (fig. S9). These results show that strong evolution of heat through ammonia adsorption onto RuO$_2$/γ-Al$_2$O$_3$ increases the catalyst bed temperature to the catalytic autoignition temperature of ammonia combustion and subsequently initiates oxidative
decomposition of ammonia. On this catalyst, adsorption sites, such as Lewis acid sites, were formed by dehydration during He pretreatment. He pretreatment at 300°C was considered necessary to form many ammonia adsorption sites to sufficiently heat the catalyst during the triggering test. In contrast, the catalytic autoignition temperature for the Ru/La2O3 catalyst was similarly determined to be 120°C (Fig. 5B), which is much higher than the maximum catalyst bed temperature (53°C) achieved for exposure of the catalyst to NH3/He gas. Hence, the heat generated by ammonia adsorption was insufficient to heat RuO2/La2O3 to its catalytic autoignition temperature, and as a result, oxidative ammonia decomposition was not triggered at room temperature.

Cycle and long-term tests for triggering oxidative decomposition of ammonia

Cycle tests for triggering oxidative decomposition of ammonia (Fig. 1) were carried out. The procedure for the cycle tests is shown in fig. S10. Before the first cycle, the RuO2/γ-Al2O3 catalyst was pretreated with He at 300°C, and oxidative decomposition of ammonia was subsequently triggered at room temperature (Fig. 6). After 35 min, the reaction was terminated by substitution of He for the NH3/O2/He mixture, and the catalyst was cooled to room temperature. O2 was then briefly supplied over the catalyst to oxidize the Ru metal formed during the reaction, and an NH3/O2/He mixture was fed to the catalyst. This O2 was added to the catalyst to eliminate the contribution of heat produced by RuO2 oxidation during exposure of the reactant to the catalyst in the second cycle (that is, O2 passivation; fig. S10); in practical applications, the cycles can be repeated without O2 passivation. This purge-feed sequence was repeated three more times. For all cycles, the oxidative decomposition of ammonia was repeatedly triggered at room temperature, and O2 was consumed completely: N2 yield was 93% and hydrogen yield was near the maximum value. After the second cycle, ammonia was apparently desorbed in situ (self-regeneration of NH3 adsorption sites) during the oxidative decomposition of ammonia. The catalyst temperature exceeded 300°C (Fig. 2C), which was sufficient to desorb ammonia from the catalyst. The reaction was triggered repeatedly despite the catalyst being exposed to O2 for O2 passivation at room temperature. These results demonstrate the essential merits of self-heating by ammonia adsorption on the catalyst compared with heat generation through oxidation of the catalyst. In the latter case, the process can no longer be rebooted when O2 in air is supplied to the reactor. Furthermore, the activity of the RuO2/γ-Al2O3 catalyst was stable for 100 hours (Fig. 7). Although Ru could be oxidized and vaporized as RuO4 under the reaction conditions, x-ray fluorescence measurements revealed that the ratio of Ru to Al in the catalyst was not changed before or after long-term reactions or after the cycle tests (table S4).

DISCUSSION

Our findings indicate that ammonia adsorption onto a RuO2/acidic medium (for example, γ-Al2O3) catalyst at room temperature is a trigger
for the oxidative decomposition of ammonia. To heat the catalyst to the catalytic ammonia autoignition temperature, we successfully used the heat evolved by ammonia adsorption onto RuO$_2$/γ-Al$_2$O$_3$. With a supply of only ammonia and O$_2$ to the catalyst at room temperature, this process can produce hydrogen along with nitrogen and water vapor; the process requires neither an external energy source nor the use of any complex procedures. Therefore, we envisage a low-carbon society using hydrogen, in which ammonia plays a role as an energy and hydrogen carrier. This study demonstrates the concept of self-heating of catalysts by adsorption of reactant molecules, which is a novel strategy for the cold-start process for hydrogen production from ammonia and other reactions. Furthermore, the heat produced via our process can be used for efficient internal heating of many devices requiring rapid initiation. We expect that our approach will lead to the development of a new technological discipline in chemical and energy science.

**MATERIALS AND METHODS**

**Catalyst preparation**

The La$_2$O$_3$ support was prepared at room temperature by adding an aqueous solution of La(NO$_3$)$_3$·6H$_2$O (Wako Pure Chemical Industries) to a solution of 25 weight % aqueous ammonia (36). The precipitate was kept in suspension by stirring overnight and was subsequently filtered, washed with distilled water, and dried at 70°C. γ-Al$_2$O$_3$ (Sumitomo Chemical Company Ltd.) and La$_2$O$_3$, which was prepared in our laboratory, were calcined for 5 hours at 700°C. RuO$_2$/γ-Al$_2$O$_3$ and RuO$_2$/La$_2$O$_3$ were then prepared by the wet impregnation method described.
in a previous report, Murata et al. (37). The mass fraction loading of Ru was set to 5% relative to the mass of the catalyst. The supports were impregnated with Ru₃(CO)₁₂ (Tanaka Kikinzoku Kogyo) in tetrahydrofuran and stirred overnight; the solvent was then removed using a rotary evaporator, and the catalyst powders were finally dried at 70°C. The obtained powder was treated in flowing He at 350°C for 5 hours to remove the CO ligand from the Ru precursor. The specific surface areas and CO chemisorption capacities, which are indicators of Ru dispersion on the catalyst, are shown in table S3.

**Triggering tests**

The catalyst powders were pressed into pellets at 52 MPa, crushed, and sieved to grains with diameters between 250 and 500 μm. The lower part of a tubular quartz reactor (inner diameter, 7 mm) was filled with α-Al₂O₃ balls and then packed with quartz wool. Then, 200 mg of catalyst was loaded onto the α-Al₂O₃ balls (fig. S4). Type K thermocouples (ø 0.5 mm) were inserted into the catalyst bed from the bottom. Research-grade gas from a high-pressure cylinder was used as the gas supply. A typical experimental procedure is shown in fig. S3. The catalysts were pretreated in pure He (50 ml min⁻¹), typically to 300°C, with a ramping rate of 10°C min⁻¹. They were then maintained for 30 min at the target temperature and subsequently cooled to room temperature (−25°C) under He. The heater of the furnace was then switched off, the furnace was opened, and the quartz reactor was wrapped with a ceramic insulation material to reduce heat loss for the subsequent reaction. The tests were then carried out under quasi-adiabatic conditions (fig. S4). An NH₃/O₂/He gas mixture, in which the typical NH₃/O₂ molar ratio was 4.1 (NH₃/O₂/He ratio, 150:37.5:20.8 ml min⁻¹; GHSV, 62.5 liters hour⁻¹ gcat⁻¹), was then fed at room temperature to the catalyst. We set the gas composition assuming the following reaction: NH₃ + 0.25 O₂ → H₂ + 0.5N₂ + 0.5H₂O. The composition of the exit gas was constantly monitored with a quadrupole mass spectrometer (M-2010QA-TDM, CANON ANELVA), which was connected to the exit of the reactor. The exit gas was then passed through an H₂SO₄ (9 M) trap to remove ammonia and a cold trap to remove water. After 30 min, the composition of the dried exit gas was analyzed with a thermal conductivity detector (GC-8A, Shimadzu). The measurable temperature range with this system is 200° to 900°C.

**Measurement of catalyst bed temperature**

During the triggering tests, changes in the temperature at the inlet of the catalyst bed were monitored using the thermocouple attached to the catalyst bed (fig. S4). Furthermore, the temperature distribution of the catalyst bed were monitored using the thermocouple attached to the catalyst, are shown in fig. S5. The measurable temperature range with this system is 200° to 900°C.

**Microcalorimetry**

Microcalorimetry was carried out using a Calvet-type heat-flux calorimeter (C-80, Setaram Instrumentation) attached to a volumetric gas adsorption analyzer (BELSORP-max, MicrotracBEL). The catalyst (100 mg) in the sample cell was pretreated in pure He at 300°C for 30 min, cooled to 50°C, and evacuated at 50°C using a turbomolecular pump. Then, 11 μmol of ammonia was gradually added to the sample cell at 50°C. The differential heat was detected by heat-flux transducers arranged in series around a reference cell and the sample cell (38). Measurements of the differential heat were performed by integrating the heat response as a function of time.

**Characterization of the supported Ru catalysts**

X-ray diffraction, x-ray photoelectron spectroscopy, HAADF-STEM, NH₃ TPD, N₂ adsorption, CO chemisorption, and x-ray fluorescence analyses were used to characterize the supported RuO₂ catalysts. Details for these methods are given in the Supplementary Materials.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/4/e1602747/DC1

**Procedures for characterizing the catalysts**

fig. S1. Conversions and yields for oxidative decomposition of ammonia (eq. 2) calculated from thermodynamics with HSC Chemistry 6.1.

fig. S2. Characterizations of RuO₂/γ-Al₂O₃.

fig. S3. Typical experimental procedure for triggering tests using heat produced by adsorption of ammonia on the catalyst.

fig. S4. Schematic of the quasi-adiabatic reactor with a quadrupole mass spectrometer (QMS) and gas chromatograph (GC).

fig. S5. Experimental setup for observing the temperature distribution of the catalyst bed.

fig. S6. Trends of MS peak intensities during triggering tests over RuO₂/γ-Al₂O₃ (A) and bare γ-Al₂O₃ (B). fig. S7. Triggering tests over RuO₂/γ-Al₂O₃ with three GHSVs.

fig. S8. Distribution of catalyst bed temperature measured at 300 s during triggering tests over RuO₂/γ-Al₂O₃ with three GHSVs.

fig. S9. NH₃-TPD profiles of RuO₂/γ-Al₂O₃ (solid lines) and bare γ-Al₂O₃ (dashed lines).

fig. S10. Experimental procedure used for five cycles of testing.

table S1. Conversions of ammonia and oxygen and yields of hydrogen during triggering tests over RuO₂/γ-Al₂O₃ at three GHSVs.

table S2. Proportions of converted NH₃ and O₂ and percentage yields of hydrogen during triggering tests over RuO₂/γ-Al₂O₃ with various NH₃/O₂ molar ratios in the feed gas.

table S3. Physicochemical properties of the catalysts.

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Carbon-free \( \text{H}_2 \) production from ammonia triggered at room temperature with an acidic \( \text{RuO}_2 / \gamma - \text{Al}_2\text{O}_3 \) catalyst

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