Metal Ruthenate Perovskites as Heterogeneous Catalysts for the Hydrolysis of Ammonia Borane

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Supporting Information

ABSTRACT: Ammonia borane (NH₃-BH₃) is of interest as a hydrogen storage material because of its ease of use and its ability to release three molar equivalents of H₂(g) via catalytic hydrolysis. Most heterogeneous catalysts for ammonia borane hydrolysis are nanoparticles containing expensive noble metals. Here, we show that metal ruthenate perovskites function as active and durable catalysts for ammonia borane hydrolysis. As a bulk powder, CaRuO₃ catalyzes the hydrolysis of ammonia borane at room temperature and is recyclable and reusable. CaRuO₃ facilitates the release of H₂(g) from aqueous ammonia borane solutions at comparable rates to some other heterogeneous catalyst systems while having a low noble metal content. Other ruthenium-based perovskites, including SrRuO₃, Ca₂LaRuO₆, Sr₂CoRuO₆, and SrLaCoRuO₆, are similarly active catalysts for room-temperature ammonia borane hydrolysis.

INTRODUCTION

Hydrogen gas is a useful energy carrier that can be produced via environmentally benign processes, burns cleanly, and has a gravimetric energy density that is several times higher than that of fossil fuels.¹ For use in vehicles, the on-board hydrogen storage targets set by the U.S. Department of Energy (DOE) state that vehicles should be capable of storing enough hydrogen to enable a driving range of >300 miles and that vehicles should be capable of storing enough hydrogen to enable a driving range of >300 miles and that hydrogen storage systems should have a gravimetric capacity of 7.5 wt % hydrogen.¹² Compression or liquefaction of hydrogen are possible solutions, but the large resource requirements and transportation costs render them unfavorable.¹ Alternatively, high temperature and pressure.⁷ Ammonia borane contains 19.6 wt % hydrogen and can release 2 molar equivalents of hydrogen and requires high temperatures to function.⁷ Solvolytic and protic solvents via catalytic methanolysis or hydrolysis can afford 3 molar equivalents of hydrogen and can occur at room temperature.⁷

Ideal catalysts for the hydrolysis of ammonia borane should be highly active, recyclable, and composed primarily of Earth-abundant, low-cost elements.² While nanoparticles of 3d transition metals such as Ni,⁸–¹⁰ Fe,¹¹ and Co¹² catalyze ammonia borane hydrolysis, the most active catalysts are currently composed of noble metals, including Pt, Pd, Rh, and Ru.¹³–¹⁵ The noble metal content can be diluted via alloying with first-row transition metals, producing more cost-effective catalysts with only slight decreases in activity. For example, nanoparticles of CoPd,¹⁶ NiRu,¹⁷ and M–Pt (M = Fe, Co, and Ni),¹⁸ are both highly active and recyclable, although they still contain up to 75 wt % of noble metals. Other classes of highly active catalysts include metal phosphides¹⁹,²⁰ and nanostructured oxides,²¹,²² as well as homogeneous ammonia borane dehydrogenation catalysts that contain ruthenium or other noble metals.²³ The identification of new classes of catalytic materials for ammonia borane hydrolysis continues to be an important research goal.

The mechanisms by which catalysts for ammonia borane hydrolysis function have been extensively studied.⁷,¹⁹ While different catalysts can proceed through different pathways, several studies and observations provide insights that are useful for considering candidate systems. For example, Ru nanoparticles, which are among the most highly studied heterogeneous catalysts for ammonia borane hydrolysis, are prone to surface oxidation.²⁴ This, coupled with enhancements in catalytic performance observed for oxide-supported Ru nanoparticles,²⁵ suggests that ruthenium-based oxide materials may be interesting candidates. At the same time, complexes of Ca and Mg are known to facilitate dehydrocoupling of the related dimethylamineborane molecule, with the alkaline earth metal centers participating in B–H and N–H bond-breaking processes.²⁶ Given these considerations, mixed metal ruthenates containing alkaline earth metals may be of interest as...
potential candidate materials for evaluating as heterogeneous catalysts for ammonia borane hydrolysis to produce molecular hydrogen. Such metal ruthenates include CaRuO$_3$, SrRuO$_3$, Ca$_2$LaRuO$_6$, Sr$_2$CoRuO$_6$, and Sr$_2$LaCoRuO$_6$ which have been studied for their magnetic and electronic properties. We show here that these perovskite-type metal ruthenates function as heterogeneous catalysts for the room-temperature hydrolysis of ammonia borane.

**RESULTS AND DISCUSSION**

CaRuO$_3$ and SrRuO$_3$ were synthesized by a coprecipitation method that involved dissolving appropriate metal salts in water, adding 3 M KOH, and heating the washed and dried precipitates at 600–900 °C for 24 h. Ca$_2$LaRuO$_6$, Sr$_2$CoRuO$_6$, and Sr$_2$LaCoRuO$_6$ were synthesized by bulk solid-state reactions of appropriate metal carbonates and oxides. Powder X-ray diffraction (XRD) data for CaRuO$_3$, SrRuO$_3$, Ca$_2$LaRuO$_6$, Sr$_2$CoRuO$_6$, and Sr$_2$LaCoRuO$_6$ are shown in Figure 1. Comparison of the experimental XRD patterns with the simulated patterns generated from published crystallographic data indicates that all five compounds are phase pure without observable crystalline impurities. The crystal structure for CaRuO$_3$, a representative example, is also shown in Figure 1. CaRuO$_3$ and SrRuO$_3$ form GdFeO$_3$-type perovskites with tilted and distorted octahedra. The related Ca$_2$LaRuO$_6$ perovskite exhibits crystallographic ordering of the Ca and Ru cations, while Sr$_2$CoRuO$_6$ and Sr$_2$LaCoRuO$_6$ have disordered arrangements of the Co and Ru cations. Scanning electron microscopy (SEM) images of the CaRuO$_3$, SrRuO$_3$, Ca$_2$LaRuO$_6$, Sr$_2$CoRuO$_6$, and Sr$_2$LaCoRuO$_6$ powders are shown in Figures 2 and S1. All polycrystalline powders had grain sizes in the range of several hundred nanometers to several micrometers.

The activities of the as-synthesized metal ruthenate powders for catalyzing the hydrolysis of ammonia borane were measured at room temperature (approx. 22 °C) in ultrapure water. RuO$_2$ was synthesized (Figure S2) and tested for comparison; Pt/C, a known catalyst for ammonia borane hydrolysis, was also tested.

![Figure 1. Left: Powder XRD data for CaRuO$_3$, SrRuO$_3$, Ca$_2$LaRuO$_6$, Sr$_2$CoRuO$_6$, and Sr$_2$LaCoRuO$_6$. Experimental XRD patterns are in color, and simulated patterns generated from published crystallographic data are in black. Right: Two views of the crystal structure of CaRuO$_3$.](image1)

![Figure 2. SEM image of the as-synthesized polycrystalline CaRuO$_3$ powder. The scale bar is 2 μm.](image2)

![Figure 3. Plot showing the number of moles of H$_2$(g) produced per mole of NH$_3$BH$_3$ vs time from ammonia borane hydrolysis catalyzed by CaRuO$_3$. Pt/C and RuO$_2$ are also shown for comparison.](image3)
yet available, would significantly increase the surface area and therefore the density of exposed active sites and the TOF.\textsuperscript{14} We note that we cannot unequivocally rule out the possibility that the H\(_2\)\( (g) \) produced from ammonia borane hydrolysis reacts with the surface of CaRuO\(_3\) to produce Ru nanoparticles. However, control experiments suggest that the observed catalytic activity is indeed due to CaRuO\(_3\) and not Ru(0) species. X-ray photoelectron spectra indicated that no zero-valent ruthenium species were present on the surface of a CaRuO\(_3\) sample that was recovered after several catalytic cycles, and SEM coupled with energy dispersive X-ray spectroscopy indicated the homogeneous incorporation of Ru and Ca throughout, without observable segregation (Figure S3).

Recyclability studies of the CaRuO\(_3\) catalyst, evaluated by repeatedly injecting fresh ammonia borane solutions, are shown in Figure 4. CaRuO\(_3\) maintained high activity for complete ammonia borane hydrolysis over five cycles, exhibiting only a 5.1% decrease in the rate of the hydrolysis reaction, which is consistent with the recyclability behavior of other known ammonia borane catalysts.\textsuperscript{21} Complementary studies where CaRuO\(_3\) was recovered and reused for five successive cycles showed similar behavior; complete hydrolysis was observed over all cycles, and TOF values were comparable. The activation energy required for CaRuO\(_3\) to catalyze the hydrolysis of ammonia borane was determined by measuring the reaction rates at several reaction temperatures while keeping all other parameters constant (Figure S4). The activation energy (\( E_a \)) for CaRuO\(_3\)-catalyzed ammonia borane hydrolysis, calculated from the Arrhenius plot in Figure S5, was 34 kJ/mol. This activation energy is comparable to those of Ru nanoparticles,\textsuperscript{15} Ru nanoparticles supported on carbon nanotubes,\textsuperscript{14} NiRu nanoparticles supported on TiO\(_2\),\textsuperscript{17} CoRu nanoparticles supported on Ti\(_3\)C\(_2\)X\(_2\) (X \( = \) OH\(^-\), F\(^-\)),\textsuperscript{35} Ni\(_{10}\)P\(_{10}\),\textsuperscript{33} and Cu\(_{10}\)O\(_{12}\)O supported on graphene oxide, which range from 12.7 to 45.5 kJ/mol.\textsuperscript{21}

Other metal ruthenates were also found to be active catalysts for ammonia borane hydrolysis (Figure S5). SrRuO\(_3\) catalyzes the hydrolysis of ammonia borane at an average rate of 3.5 mL/min and with a TOF of 3.1 mol\( (H_2) \) mol\( ^{-1} \) (SrRuO\(_3\))\(^{-1} \) min\(^{-1}\). Ca\(_2\)LaRuO\(_6\), SrCoRuO\(_6\), and SrLaCoRuO\(_6\) catalyze ammonia borane hydrolysis at average rates of 6.5, 2.3, and 1.7 mL/min, respectively. The corresponding TOF values, again calculated for low surface area bulk materials, are 5.8 mol\( (H_2) \) mol\( ^{-1} \) (SrCoRuO\(_6\))\(^{-1} \) min\(^{-1}\), 2.2 mol\( (H_2) \) mol\( ^{-1} \) (Ca\(_2\)LaRuO\(_6\))\(^{-1} \) min\(^{-1}\), and 1.5 mol\( (H_2) \) mol\( ^{-1} \) (SrLaCoRuO\(_6\))\(^{-1} \) min\(^{-1}\), respectively.

While the active sites and the mechanism by which the metal ruthenates catalyze ammonia borane hydrolysis are not yet known, the alkaline earth metals and transition metals both appear to play a role in achieving the observed catalytic performance, given the significantly higher activity of the metal ruthenates relative to RuO\(_2\) despite similar crystallinity, grain size, and surface area. This is reasonable, given the known role of oxide supports and Lewis acidic metals in promoting and enhancing catalysis in noble metal systems,\textsuperscript{36} as well as the role that calcium can play in facilitating the breaking of B–H and N–H bonds in dehydrocoupling of dimethylamineborane.\textsuperscript{26}

\section*{CONCLUSIONS}

In conclusion, CaRuO\(_3\), SrRuO\(_3\), Ca\(_2\)CoRuO\(_6\), SrLaRuO\(_6\), and SrLaCoRuO\(_6\) have been identified as catalysts for the hydrolysis of ammonia borane. Efforts to increase their surface areas, active site densities, and TOFs through nanostructuring are anticipated to further increase their rates of hydrolysis. Additionally, other families of complex oxide materials, which combine multiple metals with synergistic functions and that contain little or no noble metals, may be viable candidates to explore as heterogeneous catalysts for ammonia borane hydrolysis.

\section*{METHODS}

\textbf{Materials.} LaCl\(_3\)·7H\(_2\)O (Alfa Aesar), SrCl\(_2\)-6H\(_2\)O (Alfa Aesar), SrCO\(_3\) (Alfa Aesar), CaCO\(_3\) (Alfa Aesar), BaCO\(_3\) (Alfa Aesar), Co\(_3\)O\(_4\) (Alfa Aesar), La\(_2\)O\(_3\) (Alfa Aesar), CaCl\(_2\)-2H\(_2\)O (EM Science), RuCl\(_3\)-xH\(_2\)O (Sigma-Aldrich), borane ammonia complex (Sigma-Aldrich), Pt/C (E-TEK Inc.), and KOH (VWR) were used as received without further purification. Nanopure water (18 M\( \Omega\)) was obtained from a Barnstead Nanopure Analytical Ultrapure water system.

\textbf{Synthesis.} CaRuO\(_3\) and SrRuO\(_3\) were synthesized via coprecipitation and annealing.\textsuperscript{33} Stoichiometric amounts of the chloride salts were dissolved in ultrapure water and stirred using a magnetic stir bar for 5 min. Then, 5 mL of 3 M KOH(aq) was added to the solution, and the pH was verified to be above 13. After stirring for 1 h, the solution was allowed to stand for 2–3 h and was then subsequently washed with

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Recyclability study over five cycles of adding a fresh aqueous ammonia borane solution every 13 min to the CaRuO\(_3\) catalyst. The plot shows the number of moles of H\(_2\)\( (g) \) produced per mole of NH\(_3\)BH\(_3\) vs time.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5}
\caption{Plot showing the number of moles of H\(_2\)\( (g) \) produced per mole of NH\(_3\)BH\(_3\) vs time from ammonia borane hydrolysis catalyzed by SrRuO\(_3\), Ca\(_2\)LaRuO\(_6\), SrCoRuO\(_6\), and SrLaCoRuO\(_6\).}
\end{figure}
ultrapure water via centrifugation. The resulting black precipitate was dried and then heated in a muffle furnace for 24 h at 900 °C for CaRuO₃ and 24 h at 600 °C for SrRuO₃. Sr₂CoRuO₆ was synthesized by grinding stoichiometric amounts of SrCO₃ with Co₃O₄ and RuO₂ in a mortar and pestle for 15 min. Subsequently, the ground powder was pressed into a pellet and heated to 900 °C for 12 h, 1025 °C for 36 h, and 925 °C for 17 h, with intermittent grinding steps. Ca₃LaRuO₆ was obtained by grinding stoichiometric amounts of CaCO₃ and La₂O₃ with RuO₂ in a mortar and pestle for 15 min. Subsequently, the ground powder was pressed into a pellet and heated to 900 °C at a rate of 15 °C/min. After 12 h, the furnace was turned off and allowed to cool to room temperature. SrLaCoRuO₆ was synthesized in an identical manner, except stoichiometric amounts of SrCO₃, La₂O₃, Co₃O₄, and RuO₂ were used. RuO₂ was used by annealing RuCl₃ in air for 24 h at 600 °C.

**Materials Characterization.** Powder XRD patterns were collected with a Bruker AXS D8 ADVANCE diffractometer with Cu Kα radiation and a LynxEye 1-D detector. Simulated XRD patterns were generated with the CrystalMaker/CrystalDiffract software package using published crystallographic data for each phase (see refs. [27, 36]). SEM images were acquired using a FEI NanoSEM at an accelerating voltage of 7 keV and a working distance of 5.0 nm. Prior to imaging, a 10 nm iridium coating was sputtered using a Leica EM ACE600 high vacuum coater. Surface area measurements were performed on an ASAP 2020 Automated Surface Area and Porosimetry System using N₂ gas. Energy-dispersive spectroscopy data and elemental mapping images were collected at an accelerating voltage of 20.0 keV and a working distance of 5 mm. X-ray photoelectron spectroscopy (XPS) experiments were performed using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al Kα X-ray source (hν = 1486.7 eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter-cleaned Cu foil (Cu 2p₃/2 = 932.7 eV, Cu 2p₁/₂ = 751.1 eV). Peaks were charge-referenced to the B₃O₃ band in the boron 1s spectra at 193.0 eV. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3–6 nm (95% of the signal originated from this depth or shallower).

**Catalysis.** An aqueous solution of ammonia borane was prepared by dissolving 1 mmol of ammonia borane in 2.4 mL of ultrapure water. This solution was then injected into a 50 mL round-bottom flask that contained 0.050 mmol of the catalyst. Released H₂(g) was collected and measured over time using an inverted 100 mL graduated cylinder until the hydrolysis reaction reached completion. Rates were calculated by determining the slope of H₂(g) production as a function of time over the linear region. The data were normalized to account for any preexisting air bubbles in the graduated cylinder. All catalysts were first activated by injecting the ammonia borane solution in four separate trials. Activation energies were determined from data obtained by catalytically hydrolyzing ammonia borane at room temperature (≈22 °C), 35, 45, and 55 °C. Reactibility tests were performed by injecting fresh ammonia borane solutions without purification of the catalyst. The production of H₂(g) was confirmed by gas chromatography via a Shimadzu 2014 System GC equipped with a Haysep Q and a Carboxen 1000 column.

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