

# *Ruthenium-loaded montmorillonite as a nanocatalyst for efficient hydrogen evolution*

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**Abstract:** The global energy crisis and environmental pollution issues have intensified the search for clean and sustainable energy sources. Hydrogen, with its high energy density and clean combustion, is considered an ideal energy carrier. However, the safe and efficient storage and transportation of hydrogen pose significant challenges. Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>) has emerged as a promising hydrogen storage material due to its high hydrogen content, stability, and solubility in polar solvents. Despite its potential, the release of hydrogen from ammonia borane requires effective catalysis to overcome kinetic barriers and minimize the formation of undesirable by-products. In this study, we report the synthesis of ruthenium-loaded montmorillonite (Ru/MMT) nanocatalysts through a wet impregnation method, followed by hydrogen reduction. The Ru/MMT nanocatalysts facilitate rapid complete hydrolysis of ammonia borane, yielding over 70 mL of hydrogen in 2.5 minutes at ambient temperature, achieving a turnover frequency (TOF) exceeding 400 mol<sub>H<sub>2</sub></sub> mol<sub>Ru</sub><sup>-1</sup> min<sup>-1</sup>. Moreover, these catalysts exhibit remarkable stability across numerous cycles. This research underscores the potential of Ru/MMT nanocatalysts for effective hydrogen production from ammonia borane, offering a promising avenue for the development of sustainable hydrogen storage and release technologies.

## 1. Introduction

The global energy crisis and environmental pollution issues have intensified the search for clean and sustainable energy sources.[1, 2] Hydrogen, with its high energy density and clean combustion, is considered an ideal energy carrier.[3] However, the safe and efficient storage and transportation of hydrogen pose significant challenges.[4] Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB) has emerged as a promising hydrogen storage material due to its high hydrogen content, stability, and solubility in polar solvents.[5, 6] Despite the molecular dihydrogen bonds, the hydrolysis reaction is relatively stable under neutral and weakly alkaline conditions, making high-rate hydrolysis feasible only in the presence of appropriate catalysts.[7]

In recent years, various nanocavity-supported metal catalysts have demonstrated excellent catalytic activity and durability for hydrogen production from ammonia borane hydrolysis, yet practical applications face challenges such as high synthesis costs and environmental concerns

associated with solvent use.[8-10] Natural montmorillonite (MMT), with its low cost, abundant availability, and unique two-dimensional layered structure, proves to be an ideal support for anchoring ruthenium nanoparticles.

Herein, the ruthenium-loaded montmorillonite (Ru/MMT) nanocatalyst was prepared by simple impregnation method. Characterization with X-ray powder diffraction (XRD), inductively coupled plasma atomic emission spectrometry (ICP-AES), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) confirmed the successful incorporation of ruthenium nanoparticles. Under ambient temperature conditions, Ru/MMT could catalyzed the complete hydrolysis of ammonia borane in just 2.5 minutes, generating more than 70 ml of hydrogen with a turnover frequency (TOF) exceeding  $400 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{Ru}}^{-1} \text{ min}^{-1}$ , significantly surpassing the performance of traditional Ru/C catalysts and comparable to that of molecular sieve-supported Ru catalysts. Furthermore, the rate of hydrogen production from ammonia borane hydrolysis can be further increased with temperature, thus meeting the needs under various conditions. Additionally, the catalyst's excellent stability in catalytic reactions was confirmed through cyclic reaction tests and TEM images of the recycled samples.

## 2. Method

### 2.1. Reagents and Materials

A list of the reagents and materials used in the experiments is provided, including montmorillonite (MMT) from Macklin Reagents, ruthenium chloride ( $\text{RuCl}_3$ ) and ruthenium acetate ( $\text{Ru}(\text{OAc})_3$ ) from Aladdin Reagents, and ultrapure water prepared in the laboratory. Ammonia borane (90%) was also obtained from Aladdin Reagents.

### 2.2. Synthesis of Catalysts

The synthesis method for the Ru-MMT catalyst is as follows: Initially, commercially available montmorillonite material is heated in an oven at  $100 \text{ }^\circ\text{C}$  for 5 hours to remove adsorbed water and impurity ions from its surface. Subsequently, a 0.1M solution of  $\text{RuCl}_3$  is prepared and diluted with water, followed by stirring for 10 minutes. The dried montmorillonite support is then added to the diluted  $\text{RuCl}_3$  solution and stirred overnight. Afterward, the mixture is centrifuged, washed with water, and dried in an oven at  $100 \text{ }^\circ\text{C}$ . Finally, the montmorillonite-supported ruthenium metal nanoparticles (Ru-MMT) catalyst is prepared through reduction with hydrogen.

The synthesis of the Ru-MMT-OAc catalyst follows a similar procedure to that of the Ru-MMT catalyst, with the only difference being the substitution of the  $\text{RuCl}_3$  solution with a  $\text{Ru}(\text{OAc})_3$  solution.

### 2.3. Characterization of Catalysts

The phase composition of the catalyst was determined by X-ray powder diffraction (XRD) using a Cu target ( $\lambda = 1.5418 \text{ \AA}$ ). The composition and content of the metal loaded on the catalyst were ascertained through Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) analysis. The morphological features and distribution of elements on the surface were characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The size and distribution of the metal nanoparticles were determined by Transmission Electron Microscopy (TEM).

## 2.4. Hydrogen Production from Ammonia Borane Hydrolysis

Initially, 50 mg of catalyst is added to a flask based on the ratio of the catalytic active sites to the reactant substrate, followed by the dispersion in 0.5 ml of ultrapure water. The temperature and stirring speed are controlled using a water bath stirrer. Subsequently, 0.5 ml of ammonia borane solution is introduced to initiate the reaction, and the volume of gas produced is recorded. Upon completion of the reaction, the performance of the catalyst is characterized by calculating the turnover frequency of the catalytic reaction.

## 3. Result and Discussion

### 3.1. Preparation and characterization of catalysts

As illustrated in Figure 1, the X-ray diffraction (XRD) patterns of the ruthenium-loaded montmorillonite (Ru/MMT) catalysts retained the characteristic peaks of montmorillonite, indicating that the overall structure of montmorillonite was preserved after ruthenium loading. The shift of the first diffraction peak towards lower angles suggests an increase in the interlayer spacing due to the incorporation of Ru atoms. Furthermore, the absence of distinct Ru peaks in the XRD patterns confirms the lack of large Ru particle agglomerates on the surface, aligning with subsequent electron microscopy characterizations. In comparison, Ru/MMT-OAc samples synthesized using ruthenium acetate as the ruthenium source exhibited XRD patterns where the position of the first diffraction peak remained consistent with that of the original montmorillonite. This consistency indicates that the interlayer spacing was not significantly altered by the loading of ruthenium acetate, suggesting that the acetate ligands influenced the coordination and aggregation behavior of the ruthenium ions, hindering their intercalation.

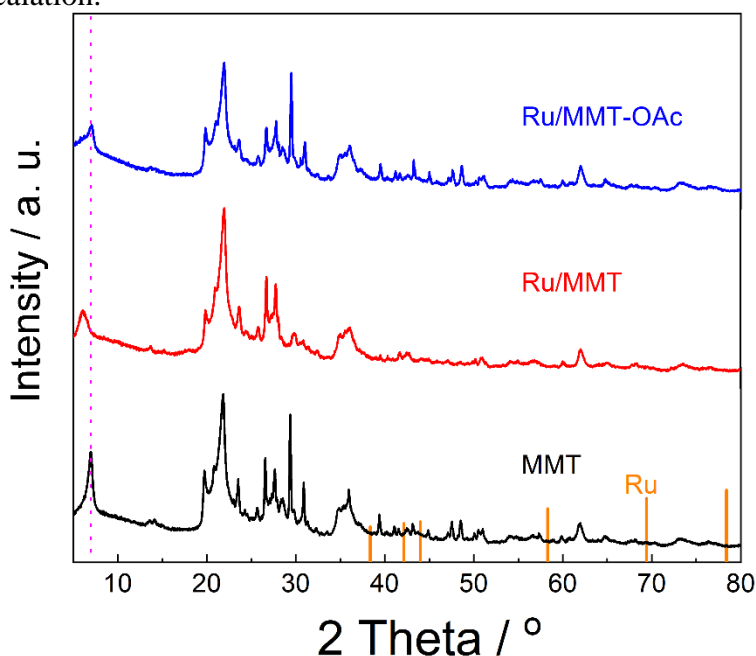


Figure 1: XRD patterns of Ru/MMT, Ru/MMT-OAc and MMT samples.

As depicted in Figure 2, the SEM images of the Ru/MMT catalysts show that the layered structure of montmorillonite was maintained after ruthenium loading, with oxide layers densely packed into larger structures. This observation, alongside the absence of large metal particle agglomerates on the surface, indicates that most of the metal was effectively encapsulated within the layered structure,

consistent with XRD findings. Energy-dispersive X-ray spectroscopy (EDX) results further revealed that the catalysts primarily consisted of silicon oxide with aluminum oxide doping, and the proportion of loaded Ru metal was minimal (Figure 2d).

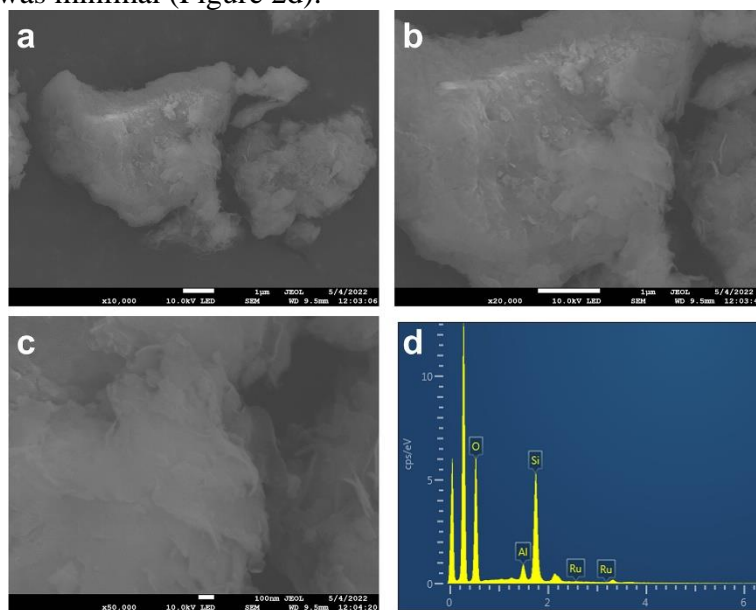


Figure 2: (a-c) SEM images and (d) EDX spectrum of Ru/MMT sample.

As depicted in Figure 3, the EEDX-mapping images reveal a uniform distribution of silicon and aluminum throughout the material, without any indication of localized elemental distribution inconsistencies. This observation is in alignment with the composite structure of silicon oxide and aluminum oxide layers in montmorillonite. Additionally, the signal for the ruthenium (Ru) element is relatively low, indicating a lower content of Ru, which corroborates the results obtained from Inductively Coupled Plasma (ICP) analysis (1.1 wt%).

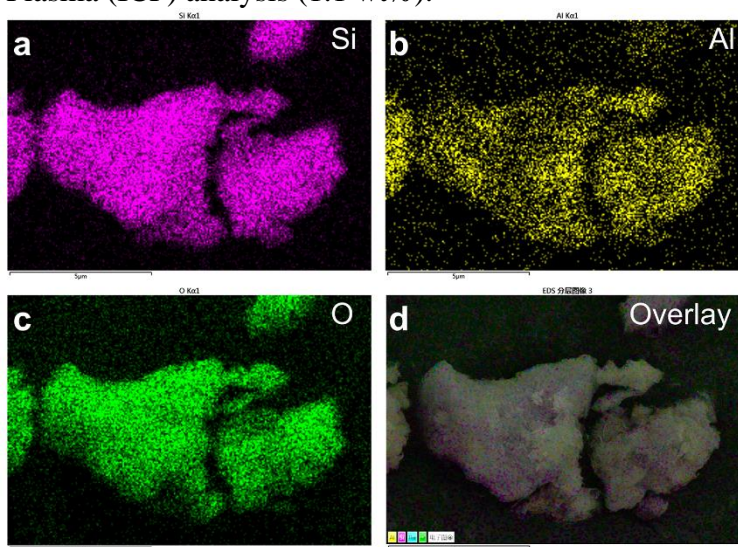


Figure 3: EDX-mapping images of Ru/MMT sample.

Figure 4 showcases TEM images revealing the typical layered structure of montmorillonite in the Ru/MMT samples, with very thin silicon and aluminum oxide layers and a thickness of just a few nanometers at the edges. Closer inspection of magnified sections highlighted the distribution of ultra-small, black particles across the montmorillonite layers, identified as Ru nanoparticles based on their

higher atomic mass compared to silicon and aluminum. The average size of these Ru nanoparticles, determined through particle size distribution analysis, was 1.8 nm, confirming the successful loading of ultra-small Ru nanoparticles onto the montmorillonite support.

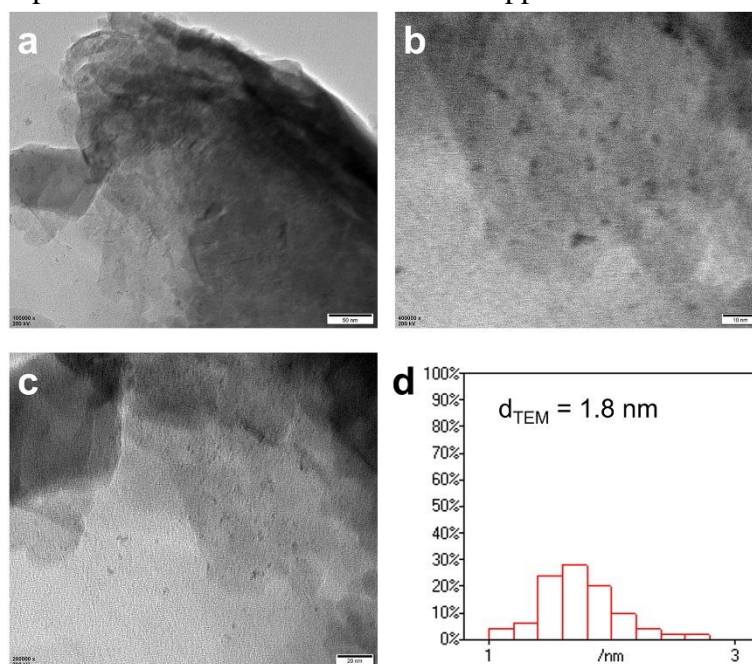


Figure 4: (a-c) TEM images and (d) size distribution of Ru/MMT sample

### 3.2. Catalytic characterization for ammonia borane hydrolysis

As depicted in Figure 5, the presence of a ruthenium catalyst facilitates the hydrolysis of ammonia borane with water, generating hydrogen gas. In contrast, montmorillonite (MMT) supports devoid of ruthenium metal produce negligible amounts of hydrogen. The Ru/MMT catalysts synthesized using ruthenium chloride exhibit exceptional catalytic performance, fully hydrolyzing ammonia borane in just 2.5 minutes at room temperature and producing over 70 ml of hydrogen, with a turnover frequency (TOF) exceeding  $400 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{Ru}}^{-1} \text{ min}^{-1}$ . This performance significantly surpasses that of traditional Ru/C catalysts ( $\text{TOF} = 46 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{Ru}}^{-1} \text{ min}^{-1}$ ) and matches the efficiency of high-performance molecular sieve Ru/SAPO-34-0.8Si catalysts ( $\text{TOF} = 490 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{Ru}}^{-1} \text{ min}^{-1}$ ).

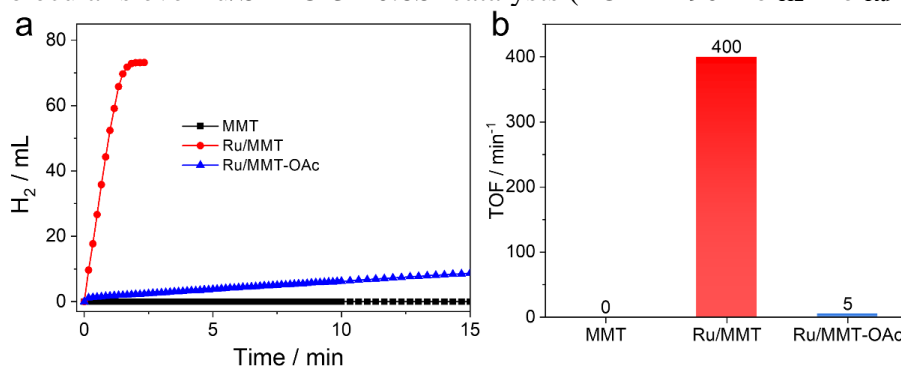


Figure 5: (a) Time course plots and (b) TOF values for AB hydrolysis at 25 °C.

As shown in Figure 6a, the rate of hydrogen production from ammonia borane hydrolysis increases noticeably with temperature, reducing the time required for complete hydrolysis. At a temperature of 30 °C, 50 mg of Ru/MMT catalyst can catalyze the production of over 70 ml of hydrogen in less than

1 minute. The calculated apparent activation energy ( $E_a$ ) is 82.1 kJ/mol, similar to that observed with traditional ruthenium catalysts. Figure 6b demonstrates that the performance of the Ru/MMT catalyst remains nearly unchanged after cyclic recycling, still producing 70 ml of hydrogen within 2 minutes. The TOF value after recycling reaches approximately  $390 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{Ru}}^{-1} \text{ min}^{-1}$ , indicating only a slight decrease of about 5% in performance, thereby confirming the catalyst's excellent stability in catalytic reactions.

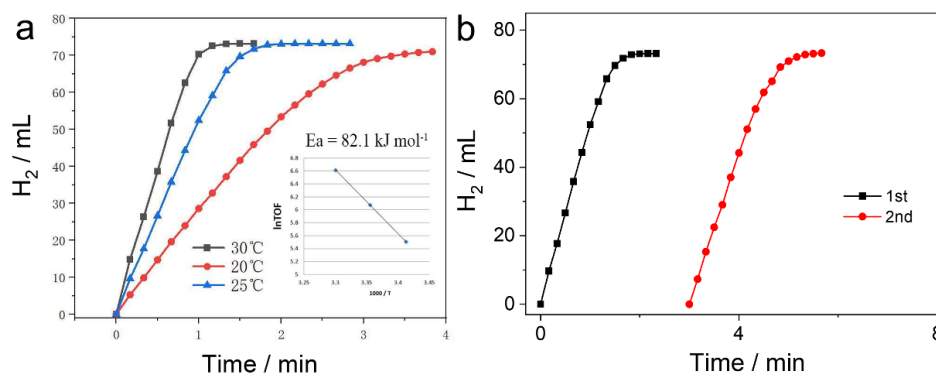


Figure 6: (a) Arrhenius plots and (b) Durability test over Ru/MMT catalyst.

Furthermore, TEM images in Figure 7 reveal that the recycled Ru/MMT samples retain the typical layered structure of montmorillonite, indicating that the support structure remains intact. Closer examination reveals that the Ru nanoparticles are uniformly distributed across the montmorillonite layers without the presence of large particles. Particle size distribution analysis shows that the average size of the Ru nanoparticles ( $d_{\text{TEM}}$ ) is 2.1 nm, larger than that in samples before catalysis, which may contribute to a slight decrease in hydrogen production efficiency. Nonetheless, the Ru nanoparticles maintain an ultra-small size, ensuring continued high catalytic performance.

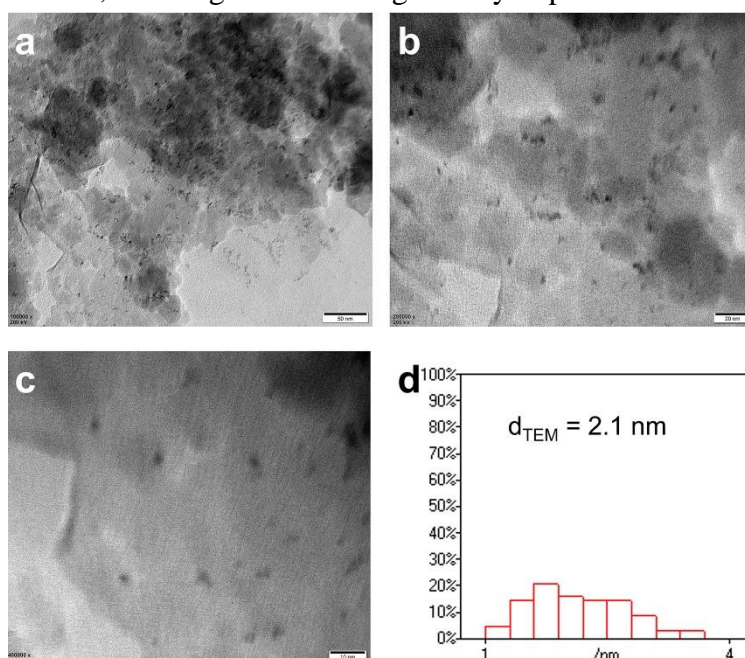


Figure 7: (a-c) TEM images and (d) size distribution of recycled Ru/MMT catalyst.

#### 4. Conclusions

This study showcases the exceptional catalytic performance of Ru/MMT nanocatalysts for

hydrogen production from the hydrolysis of ammonia borane, addressing key challenges associated with hydrogen storage and release. The use of natural montmorillonite as a support not only reduces the cost and environmental impact associated with the synthesis of nanoporous materials but also offers a scalable and efficient solution for industrial applications. The high activity, stability, and cost-effectiveness of Ru/MMT nanocatalyst highlight its potential as a sustainable solution for hydrogen storage and release technologies.

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