

UNIFORM RU NANOPARTICLES WITH MGO SUPPORTED ON BETA ZEOLITE FOR EFFICIENT HYDROGEN GENERATION FROM AMMONIA BORANE HYDROLYSIS

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Abstract: Hydrogen energy has garnered widespread attention as a key component of the future energy landscape. However, the safe storage and transportation of hydrogen remain significant challenges to its widespread adoption. Solid chemical hydrogen storage materials, such as ammonia borane, offer a promising solution by enabling safe storage under conventional conditions while allowing rapid hydrogen release in the presence of noble metal catalysts. Nevertheless, the high cost of these noble metal catalysts limits their practical application. In this study, we developed a highly dispersed Ru-based nanoparticle catalyst (< 2 nm) supported on commercial zeolites using a simple ion exchange method. This approach significantly enhances catalytic performance and increases Ru utilization, effectively reducing catalyst costs. Additionally, incorporating magnesium oxide further enhances catalytic activity, providing a feasible strategy for designing efficient hydrogen production catalysts. This work presents a cost-effective approach to advancing hydrogen energy applications.

Keywords: Metal nanoparticle; Zeolite; Hydrogen energy; Hydrogen generation; Hydrolysis reaction

1 INTRODUCTION

Hydrogen energy is increasingly recognized as a cornerstone of future clean energy systems due to its high energy density and environmentally friendly nature.[1-6] However, a significant challenge remains in the safe and efficient storage and transportation of hydrogen. Conventional methods, such as high-pressure gas storage and cryogenic systems, pose safety concerns and logistical difficulties.[7-11] Liquid chemical hydrogen storage materials, particularly ammonia borane (AB), offer a safer and more practical solution by allowing hydrogen to be stored under ambient conditions and released on-demand through catalytic processes.[12-16] While noble metal catalysts, especially Ru, are highly effective in facilitating hydrogen release from AB, their high cost and scarcity limit their widespread application.[17-20] Therefore, there is a strong demand for more efficient and cost-effective catalytic systems that reduce the reliance on noble metals without sacrificing performance.

Zeolites, as a class of highly porous materials, have gained significant attention in recent years for their ability to enhance catalytic performance through confinement effects.[21,22] The well-ordered microporous structure of zeolites, consisting of a three-dimensional network of channels and cavities, allows for the encapsulation and dispersion of metal nanoparticles, preventing their agglomeration and enhancing stability. Various studies have demonstrated the effectiveness of zeolites in stabilizing noble metal catalysts while promoting their activity.[23,24] For instance, research has shown that zeolite-supported platinum and palladium nanoparticles exhibit superior catalytic activity and stability due to the spatial constraints provided by the zeolite framework. These confinement effects ensure that the nanoparticles remain highly dispersed, increasing the available surface area for catalytic reactions and protecting them from sintering under harsh conditions. This unique property of zeolites makes them ideal candidates for supporting noble metal catalysts in hydrogen storage and production applications.[25] Building on this body of work, our study explores the potential of zeolites as a support material for highly dispersed Ru nanoparticles in hydrogen release from AB.

In this study, we developed a novel catalytic system by confining Ru nanoparticles, with a size of less than 2 nm, within the pores of commercial zeolites using a simple ion exchange method. The zeolite support effectively controls the growth and distribution of the Ru nanoparticles, ensuring a high degree of dispersion and preventing particle aggregation. This confinement effect significantly enhances the catalytic activity of Ru, as the increased surface area of the dispersed nanoparticles leads to more efficient hydrogen release from AB. Moreover, the porous structure of the zeolite provides a protective environment, improving the stability and durability of the catalyst under reaction conditions. To further improve the system's efficiency, we incorporated MgO nanoparticles as a co-catalyst. The combination of Ru confinement within the zeolite matrix and the promotional effect of MgO resulted in a highly efficient and cost-effective catalytic system for hydrogen production. This work demonstrates the potential of zeolite-based confinement strategies for optimizing noble metal catalysts and offers a promising pathway for developing advanced catalysts for hydrogen energy applications.

2 METHODS

2.1 Preparation of Catalysts

The uniform Ru nanoparticles supported on Beta zeolite were prepared by ion exchange method. Typically, 1 g of Beta zeolite ($\text{Si}/\text{Al}_2\text{O}_3 = 25$) was dissolved in 10 g of water. After adding a specific volume of RuCl_3 solution, the mixture was stirred for 2 hours. The solid formed was then washed twice with water to remove any remaining impurities. The final step involved reducing the catalyst powder under pure hydrogen at 573 K for 2 hours, resulting in the synthesis of the Ru/Beta-IE catalyst.

For the Ru-MgO/Beta catalyst, the Beta zeolite was impregnated with $\text{Mg}(\text{NO}_3)_2$ solution and calcined at 773 K before fabrication of Ru nanoparticle.

2.2 Catalytic Test

A two-necked 25 mL round-bottom flask was prepared by mixing an appropriate amount of catalyst with 0.5 mL of water. The flask was then placed in a water bath and stirred magnetically at 600 rpm, maintaining the temperature at 298 K under ambient conditions. To initiate the reaction, 0.5 mL of a 2.0 M aqueous ammonia borane (AB) solution was injected into the flask using a syringe, ensuring that the molar ratio of metal to AB remained constant. The volume of gas generated during the reaction was measured using a gas burette, while the mass changes were recorded with an electronic balance.

3 RESULTS

The preparation of the Ru/Beta-IE catalyst is visually outlined in Figure 1A. This schematic illustrates the ion exchange method used for synthesizing the catalyst. Figures 1B-D present scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HR-TEM) images of the catalyst. These images reveal that the Ru nanoparticles are uniformly dispersed on the Beta zeolite, with a particle size below 2 nm. The STEM images confirm the high dispersion and uniform size distribution of the Ru nanoparticles confined within zeolite channels, indicating successful synthesis with no aggregation, which is critical for maximizing the catalytic surface area and ensuring stability during the reaction. The HR-TEM images further demonstrates Ru nanoparticles with lattice spacing of 0.234 nm, which is attributed to crystal face (100) of Ru metal.

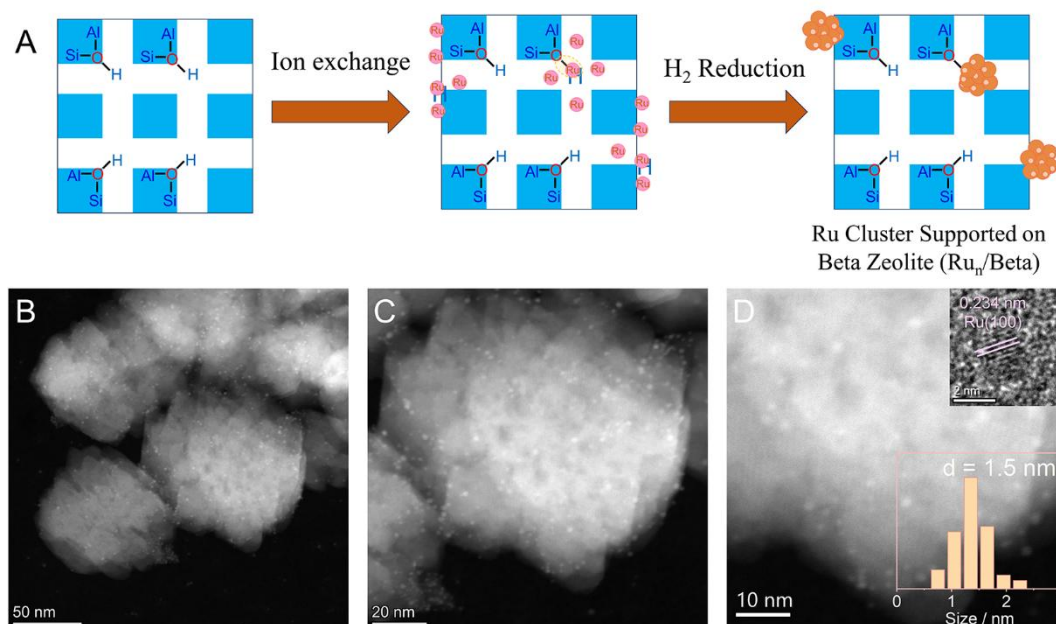


Figure 1 A Scheme for the Preparation of Ru/Beta-IE Catalyst by Ion Exchange Method. B-D STEM Images and High-resolution TEM Image for the Ru/Beta-IE Catalyst

In Figure 2A, X-ray diffraction (XRD) patterns of both the Ru/Beta-IE catalyst and the Beta zeolite are presented. The absence of distinct Ru peaks in the Ru/Beta-IE sample suggests that the Ru nanoparticles are highly dispersed and below the detection limit of the XRD, confirming their small size and high distribution. Figure 2B presents the Ru 3p X-ray photoelectron spectroscopy (XPS) spectra, highlighting the chemical state of Ru in the catalyst. The spectra indicate that Ru is predominantly present in a metallic state, which is essential for catalytic activity. Figures 2C-D provide further SEM images, demonstrating the high stability of the zeolite support, consistent with the findings in Figure 1.

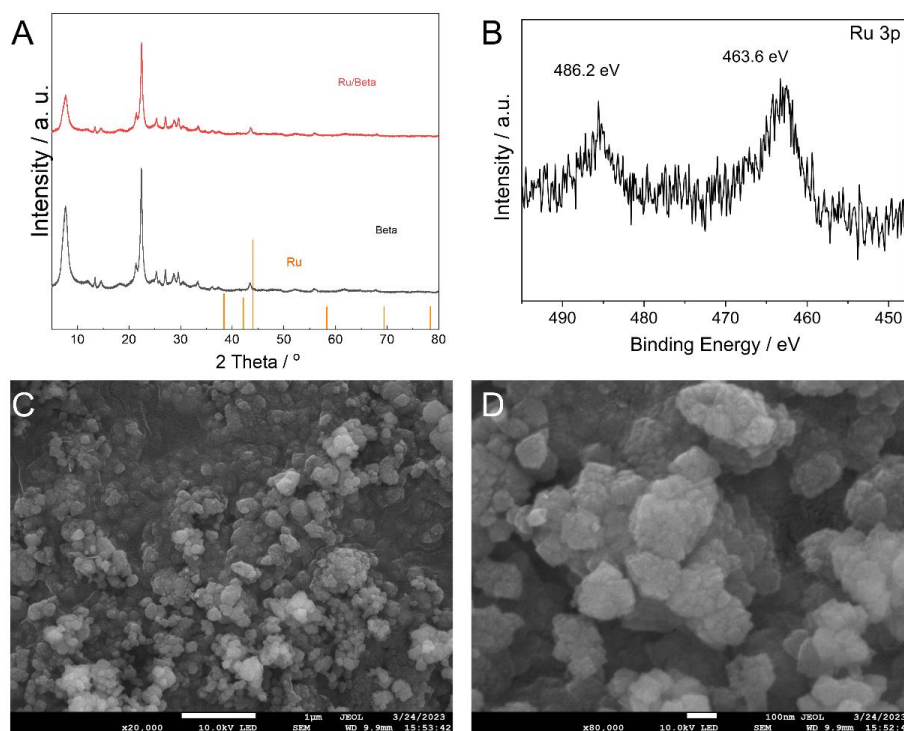


Figure 2 A XRD Patterns of Ru/Beta-IE and Beta Samples. B Ru 3p XPS Spectra for the Ru/Beta-IE Catalyst. C-D SEM Images for the Ru/Beta-IE Catalyst

In Figures 3A-B, the catalytic performance of the Ru/Beta-IE catalyst is evaluated through hydrogen generation experiments. The graphs display the volume of hydrogen released over time during the hydrolysis of ammonia borane (AB). The Ru/Beta-IE catalyst exhibits excellent activity, with rapid hydrogen release and high overall yield. This enhanced performance is attributed to the high dispersion of Ru nanoparticles and the confinement effect provided by the Beta zeolite support. The incorporation of MgO further enhances the catalytic performance, as indicated by the higher hydrogen generation rates compared to other catalysts, increasing the TOF value from 314 min^{-1} to 476 min^{-1} . This could be attributed to the increasing adsorb energy of water from 0.21 to 0.45 eV, as shown in Figure 3C, validating the effectiveness of the Ru/Beta-IE system in hydrogen production applications.

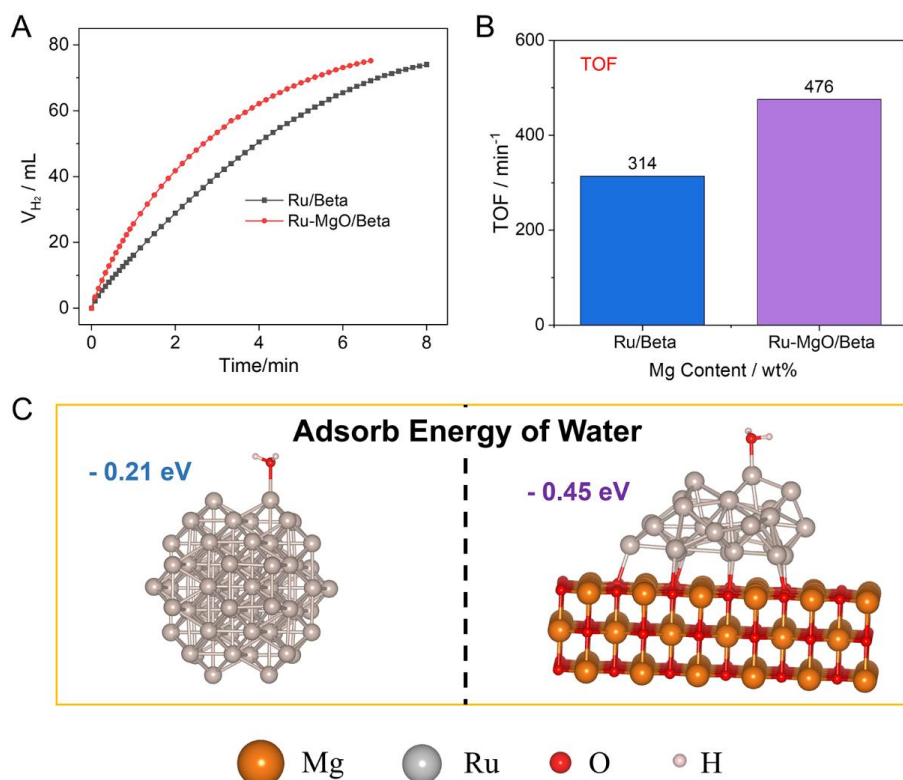


Figure 3 A-B The Catalytic Performance of the Ru/Beta-IE and Ru-MgO/Beta C-D Adsorb Energy of Water for the Ru/Beta-IE and Ru-MgO/Beta Catalyst

Figure 4 presents the analysis of the gas products generated during the catalytic hydrolysis of ammonia borane (AB) using the Ru/Beta-IE catalyst. The gas composition was analyzed using gas chromatography with a thermal conductivity detector (GC-TCD) and mass spectrometry (MS). The results confirm that the gas produced is pure hydrogen, with no detectable traces of ammonia or other by-products. This is crucial for hydrogen energy applications, as the absence of ammonia ensures the purity of the hydrogen fuel and prevents potential contamination issues in downstream processes. The high purity of the hydrogen produced further highlights the efficiency and selectivity of the Ru/Beta-IE catalyst system, making it highly suitable for practical hydrogen production applications.

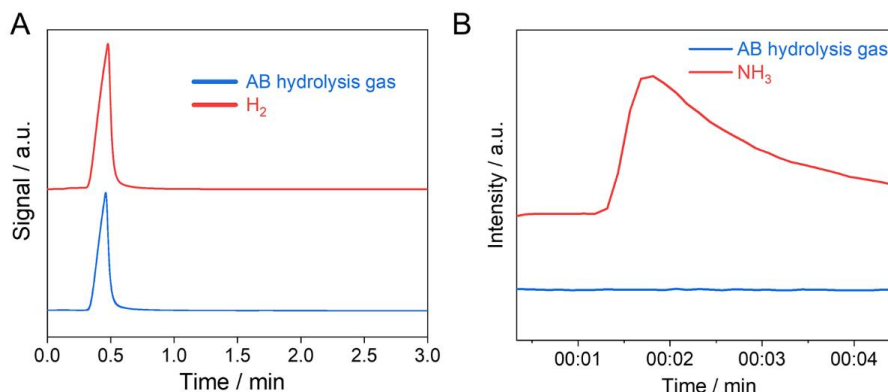


Figure 4 **A** The GC-TCD spectra of Gas Product in Ammonia Borane Hydrolysis. **B** The Mass Spectrometry of Gas Product in Ammonia Borane Hydrolysis

4 CONCLUSION

This study successfully demonstrates the potential of zeolites as effective support material for noble metal catalysts, specifically for hydrogen release from ammonia borane. By confining ruthenium nanoparticles within Beta zeolites, we achieved highly dispersed Ru particles, smaller than 2 nm, which significantly improved the catalytic performance. The zeolite's confinement effect not only enhanced the catalyst's efficiency by increasing the active surface area but also stabilized the Ru nanoparticles, preventing agglomeration and extending their durability. Additionally, the incorporation of MgO nanoparticles as a co-catalyst further boosted the system's efficiency, making it a cost-effective solution by reducing the reliance on precious metals. This work highlights the importance of utilizing porous materials like zeolites for catalyst development and opens up new possibilities for designing advanced, scalable catalytic systems for hydrogen storage and production.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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REFERENCES

- [1] Barreto, L, Makihira, A, Riahi, K. The hydrogen economy in the 21st century: a sustainable development scenario. *Int. J. Hydrogen Energy*, 2003, 28(3): 267-284. DOI: 10.1016/S0360-3199(02)00074-5.
- [2] Schlapbach, L, Züttel, A. Hydrogen-storage materials for mobile applications. *Nature*, 2001, 414(6861): 353-358. DOI: 10.1038/35104634.
- [3] Zhang, D, Wang, M, Wei, G, et al. High visible light responsive ZnIn₂S₄/TiO₂-x induced by oxygen defects to boost photocatalytic hydrogen evolution. *Appl. Surf. Sci*, 2023, 622, 156839. DOI: <https://doi.org/10.1016/j.apsusc.2023.156839>.
- [4] Guo, M, Zhan, J, Wang, Z, et al. Supercapacitors as redox mediators for decoupled water splitting. *Chin. Chem. Lett*, 2023, 34(2): 107709. DOI: <https://doi.org/10.1016/j.ccl.2022.07.052>.
- [5] Zhang, L, Cao, S, Zhang, Y, et al. Regulating lithium-ion transport route via adjusting lithium-ion affinity in solid polymer electrolyte. *Chem. Eng. J*, 2024, 479, 147764. DOI: <https://doi.org/10.1016/j.cej.2023.147764>.
- [6] Xu, H, Zhang, H, Cui, L, et al. Unravelling the synergy of platinum-oxygen vacancy in CoO_x for modulating hydrogenation performance. *Chem. Eng. J*, 2024, 488, 150841. DOI: <https://doi.org/10.1016/j.cej.2024.150841>.
- [7] Graetz, J. New approaches to hydrogen storage. *Chem. Soc. Rev*, 2009, 38(1): 73-82. DOI: 10.1039/B718842K.
- [8] Niaz, S, Manzoor, T, Pandith, AH. Hydrogen storage: Materials, methods and perspectives. *Renewable and Sustainable Energy Reviews*, 2015, 50, 457-469. DOI: 10.1016/j.rser.2015.05.011.
- [9] Bai, S, Jia, A, Song, J, et al. Metal-support interactions in heterogeneous catalytic hydrogen production of formic

- acid. *Chem. Eng. J.*, 2023, 474, 145612. DOI: <https://doi.org/10.1016/j.cej.2023.145612>.
- [10] Meng, W, Sun, S, Xie, D, et al. Engineering defective Co₃O₄ containing both metal doping and vacancy in octahedral cobalt site as high performance catalyst for methane oxidation. *Molecular Catalysis*, 2024, 553, 113768. DOI: 10.1016/j.mcat.2023.113768.
- [11] Xue, W, Zhao, B, Liu, H, et al. Ultralow Pd bimetallic catalysts boost (de)hydrogenation for reversible H₂ storage. *Appl Catal B: Environ*, 2024, 343, 123574. DOI: 10.1016/j.apcatb.2023.123574.
- [12] Yadav, M, Xu, Q. Liquid-phase chemical hydrogen storage materials. *Energy Environ. Sci*, 2012, 5 (12), 9698-9725. DOI: 10.1039/C2EE22937D.
- [13] Aardahl, CL, Rassat, SD. Overview of systems considerations for on-board chemical hydrogen storage. *Int. J. Hydrogen Energy*, 2009, 34(16): 6676-6683. DOI: 10.1016/j.ijhydene.2009.06.009.
- [14] Li, J, Cai, T, Feng, Y, et al. Subnanometric Bimetallic Pt-Pd Clusters in Zeolite for Efficient Hydrogen Production and Selective Tandem Hydrogenation of Nitroarenes. *Sci. Chi. Chem*, 2024, 67(9): 2911-2917. DOI: 10.1007/s11426-024-2132-1.
- [15] Wang, L, Li, H, Zhang, W, et al. Supported Rhodium Catalysts for Ammonia-Borane Hydrolysis: Dependence of the Catalytic Activity on the Highest Occupied State of the Single Rhodium Atoms. *Angew. Chem. Int. Ed*, 2017, 56(17): 4712-4718. DOI: 10.1002/anie.201701089.
- [16] Guan, S, Yuan, Z, Zhuang, Z, et al. Why do Single-Atom Alloys Catalysts Outperform both Single-Atom Catalysts and Nanocatalysts on MXene? *Angew. Chem. Int. Ed*, 2023, 63(4): e202316550. DOI: 10.1002/anie.202316550.
- [17] Wang, C, Astruc, D. Recent developments of nanocatalyzed liquid-phase hydrogen generation. *Chem. Soc. Rev*, 2021, 50(5): 3437-3484. DOI: 10.1039/D0CS00515K.
- [18] Xu, Q, Chandra, M. A portable hydrogen generation system: Catalytic hydrolysis of ammonia-borane. *J. Alloys Compd*, 2007, 446-447, 729-732. DOI: 10.1016/j.jallcom.2007.01.040.
- [19] Li, J, Feng, Y, Li, X, et al. Sub-2 nm Ternary Metallic Alloy Encapsulated within Montmorillonite Interlayers for Efficient Hydrogen Generation from Ammonia Borane Hydrolysis. *ACS Catal*, 2024, 14, 14665-14677. DOI: 10.1021/acscatal.4c03380.
- [20] Yang, J, Yang, Z, Li, J, et al. Engineering a hollow bowl-like porous carbon-confined Ru-MgO hetero-structured nanopair as a high-performance catalyst for ammonia borane hydrolysis. *Mater. Horiz*, 2024, 11(8): 2032-2040. DOI: 10.1039/D3MH01909H.
- [21] Zhang, K, Wang, N, Meng, Y, et al. Highly dispersed Pd-based pseudo-single atoms in zeolites for hydrogen generation and pollutant disposal. *Chem. Sci*, 2024, 15(1): 379-388. DOI: 10.1039/D3SC05851D.
- [22] Wang, J, Ma, X, Zhu, Z, et al. Pore engineering in robust carbon nanofibers for highly efficient capacitive deionization. *Sep. Purif. Technol*, 2024, 332, 125797. DOI: <https://doi.org/10.1016/j.seppur.2023.125797>.
- [23] Sun, Q, Wang, N, Yu, J. Advances in Catalytic Applications of Zeolite-Supported Metal Catalysts. *Adv. Mater*, 2021, 33(51): 2104442. DOI: <https://doi.org/10.1002/adma.202104442>.
- [24] Zhao, Z, Zhang, T, Feng, Y, et al. Subnanometer palladium-manganese clusters in hydrophilic amino-functionalized zeolites for efficient formic acid dehydrogenation. *Chem. Eng. J.*, 2024, 496, 154194. DOI: <https://doi.org/10.1016/j.cej.2024.154194>.
- [25] Sun, Q, Wang, N, Xu, Q, et al. Nanopore-Supported Metal Nanocatalysts for Efficient Hydrogen Generation from Liquid-Phase Chemical Hydrogen Storage Materials. *Adv. Mater*, 2020, 32(44): 2001818. DOI: <https://doi.org/10.1002/adma.202001818>.