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Ultrafine RhNi Nanocatalysts Confined in Hollow Mesoporous Carbons for a Highly Efficient Hydrogen Production from Ammonia Borane

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ABSTRACT: Ammonia borane (AB) has received growing research interest as one of the most promising hydrogen-storage carrier materials. However, fast dehydrogenation of AB is still limited by sluggish catalytic kinetics over current catalysts. Herein, highly uniform and ultrafine bimetallic RhNi alloy nanoclusters encapsulated within nitrogen-functionalized hollow mesoporous carbons (defined as RhNi@NHMCs) are developed as highly active, durable, and selective nanocatalysts for fast hydrolysis of AB under mild conditions. Remarkable activity with a high turnover frequency (TOF) of 1294 mol_{H₂} mol_{Rh}⁻¹ min⁻¹ and low activation energy (E_a) of 18.6 kJ mol⁻¹ is observed at room temperature, surpassing the previous Rh-based catalysts. The detailed mechanism studies reveal that when catalyzed by RhNi@NHMCs, a covalently stable O–H bond by H₂O first cleaves in electropositive H* and further attacks B–H bond of AB to



stoichiometrically produce 3 equiv of H_2 , whose catalytic kinetics is restricted by the oxidation cleavage of the O–H bond. Compositional and structural features of RhNi@NHMCs result in synergic electronic, functional, and support add-in advantages, kinetically accelerating the cleavage of the attacked H_2O (O–H bond) and remarkably promoting the catalytic hydrolysis of AB accordingly. This present work represents a new and effective strategy for exploring high-performance supported metal-based alloy nanoclusters for (electro)catalysis.

■ INTRODUCTION

One of the most critical issues involving the rapid growth of industrial production and population in the world is to search for clean and sustainable energy sources instead of traditional fossil fuels. The cleanest energy source of the future, hydrogen has received more attention for its application as highly energyefficient fuel cells.¹⁻⁴ In comparison to electrochemical water splitting, the catalytic H₂ production from the dehydrogenation of the chemical hydrogen-storage carrier materials has been attracting alternative research interests.5-8 Ammonia borane (NH₃-BH₃, AB), as one of the most promising hydrogenstorage carries due to the high hydrogen content and good stability in solid/solution states, has been widely investigated to produce H_2 under mild conditions.^{9–12} Generally, the chemical dehydrogenation of AB includes hydrolysis, methanolysis, and dehydrocoupling routes, which strongly correspond to the catalysts and solvents.^{11,13} Among them, the hydrolysis of AB in H₂O to produce 3 equiv of H₂ is more preferable. In the past two decades, vast efforts have been devoted to developing highly efficient, selective, economical, and stable catalysts for the fast H_2 production from the hydrolysis of AB.^{14–23} To date, platinum (Pt) and its alloys are

recognized as state-of-the-art catalysts for the fast hydrolysis of AB, but the sluggish kinetics (under mild conditions) still restrict their large-scale practical applications. Therefore, it is highly desirable to rationally design and explore other metal-based catalysts bearing high and selective catalytic activities for the fast dehydrogenation of AB.

Rhodium (Rh), a 4d transition metal, possesses properties similar to those of Pt, exhibiting great potential as an alternative metal catalyst material for H_2 production.^{24–31} Alloying Rh with more oxophilic 3d metals, for example, Ni and Co, can not only enlarge the utilization efficiency of precious Rh but also modify its electronic structure and introduce new functions, both of which would synergistically improve the catalytic performance in various H_2 production reactions.^{32–40} However, ultrafine Rh and its alloy nanoclusters

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Figure 1. (a) Synthetic procedures of RhNi@NHMCs. (b) SEM, (c, d) TEM, (e) scanning transmission electron microscopy (STEM), (f, g) highmagnification TEM and (h) STEM, and (i) high-resolution TEM images of RhNi@NHMCs. (j) STEM energy-dispersive X-ray spectroscopy (EDS) elemental maps of RhNi@NHMC.

(<3 nm) would be usually synthesized in the presence of organic stabilizers, which remarkably decreased the Rh active sites to the reactants and thus deactivated the catalysis. This limitation might be overcome by ligand-free Rh-based nanoclusters supported on a solid and high-surface-area matrix with a precisely desired nanostructure/morphology. Recently, hollow and mesoporous carbons (HMCs) have become promising metal catalyst supports to promote catalysis because of the large surface to uniformly encapsulate the nanoclusters and the hierarchical structure to kinetically accelerate the mass/electron transport in the reaction solution.⁴¹⁻⁴⁴ Despite many efforts, supported Rh-based alloy nanocatalysts within the HMCs have never been reported, which hinders the fundamental investigations of catalytic performance (activity, stability, and selectivity) and the corresponding mechanism for H₂ production from the dehydrogenation of AB.

Here, we report a simple self-limiting method for the encapsulation of highly uniform and ultrafine bimetallic RhNi alloy nanoclusters within nitrogen-functionalized HMCs (defined as RhNi@NHMCs) for the fast hydrolysis of AB under mild conditions. Benefiting from multiple compositional and structural advantages, RhNi@NHMCs not only display synergic electronic and functional effects that accelerate catalytic kinetics and optimize the selectivity for complete H₂ production but also expose support effects, which facilitates mass transport and stabilizes RhNi alloys. The catalytic tests indicate that RhNi@NHMCs possess a remarkably high activity with a turnover frequency (TOF) of 1294 mol_{Ha} $mol_{Rh}^{-1} min^{-1}$ and high selectivity with 3 equiv of produced H₂ related to AB at 25 °C. Mechanism tests, including the effects of AB/catalyst amounts and temperatures, kinetic isotope effect (KIE), and NaOH-promotion experiments, reveal that RhNi@NHMCs could kinetically accelerate the

oxidation cleavage of the covalently stable O–H bond in the attacked H_2O (acting as the rate-determining step) and result in the high activity and selectivity for fast H_2 production from the hydrolysis of AB. This work represents big progress for the rational design of the high-performance and supported nanocatalysts with compositional and structural synergies for the fast H_2 production from hydrogen-storage materials.

RESULTS AND DISCUSSION

The synthetic procedures of RhNi@NHMC are schematically illustrated in Figure 1a. First, the NHMC support is fabricated with the template-free⁴¹ and "soft-nitriding" methods.^{45,46} Scanning electron microscopy (SEM) shows that the obtained NHMCs are morphologically spherical with an average diameter of 320 nm. Transmission electron microscopy (TEM) exhibits they are hollow with a wall thickness of 55 nm and a hollow cavity of 210 nm (Figure S1). The highmagnification TEM further discloses that the wall framework of NHMCs is structurally mesoporous with radially opened pore channels of 7.3 nm. Subsequently, bimetallic RhNi alloys are grown in situ within the mesoporous channels of the NHMC support through an under-temperature-reductionassisted self-limiting method.⁴⁷ Typically, Rh³⁺ and Ni²⁺ are co-impregnated into the N-functionalized channels of the NHMCs based on the strong coordination interactions between metal precursors and support and then reduced in situ with H₂ at 250 °C to grow ultrafine bimetallic RhNi alloy nanoclusters.

RhNi@NHMCs with an Rh/Ni atomic ratio of 1/3 are thoroughly characterized as an example, since they exhibit the best catalytic activity for H_2 production from the hydrolysis of AB (see below). Similar to the NHMCs, RhNi@NHMCs are morphologically spherical and structurally hollow and meso-

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Figure 2. (a) SAXS patterns of NHMCs and RhNi@NHMCs. (b) N_2 sorption isotherms, (c) the corresponding pore-size distributions, and (d) XRD pattern of RhNi@NHMCs. High-resolution X-ray photoelectron spectroscopy (XPS) spectra of (e) Rh 3d and (f) Ni 2p of RhNi@NHMCs.



Figure 3. (a) Time-dependent plots of the produced H_2 and (inset) the corresponding TOF values from the hydrolysis of AB catalyzed by RhNi@ NHMCs, Rh@NHMCs, and commercial Rh/C. (b) Comparisons of the TOF values of RhNi@NHMCs with the previously reported Rh-based catalysts. (c) Calculated TOF values obtained in different Rh/Ni ratios of RhNi@NHMCs. (d) Catalytic cycling stability of RhNi@NHMCs for the H_2 production from the hydrolysis of AB. The catalytic conditions are as follows: 20 mg of AB, 2.4 mg of catalysts, 7.0 mL of H_2O , and 25 °C.

porous with very uniform distributions (Figures 1b,d and S2). This implies that the encapsulation of bimetallic RhNi alloys does not change the entire morphology and nanostructure of the NHMC support. In contrast, the high-angle annular dark-field scanning TEM (HAADF-STEM) observation exhibits numerous bright spots that are homogeneously dispersed within NHMCs, indicating the formation of bimetallic RhNi alloys (Figures 1e and S3). High-magnification TEM images further confirm the presence of the RhNi alloys (Figure 1f). Furthermore, TEM and STEM images in higher magnification disclose that RhNi alloys are homogeneously encapsulated

within the mesoporous channels of NHMCs, rather than on the surface of the nanospheres (Figure 1g,h). Bimetallic RhNi alloys are highly uniform with a diameter of 2.4 ± 0.6 nm. High-resolution TEM was also characterized, revealing that bimetallic RhNi alloys have a face-centered cubic (fcc) crystalline structure (Figure 1i). The *d*-spacing of RhNi alloys is 0.21 nm, slightly smaller than that of monometallic Rh. This confirms that Ni with a smaller atomic size is successfully alloyed with Rh. Meanwhile, STEM elemental maps display the coexistence of Rh and Ni, further implying the successful growth of bimetallic RhNi alloys within the NHMC support. pubs.acs.org/IC

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Figure 4. Time-dependent plots of the produced H_2 over RhNi@NHMCs, Rh@NHMCs, and Rh/C in (a) different AB amounts and (b) catalyst amounts. Summarizations of relationships (c) between ln TOF and ln [AB] and (d) between ln TOF and ln [Rh]. The catalytic conditions in (a) and (c) are as follows: different amounts of AB, 2.4 mg of catalysts, 7.0 mL of H_2O , and 25 °C. The catalytic conditions in (b) and (d) are as follows: 20 mg of AB, different amounts of catalysts, 7.0 mL of H_2O , and 25 °C.

The compositional ratio from STEM energy-dispersive X-ray spectroscopy (EDS) is measured to be 1:2.7 with a total loading amount of Rh of 0.96 wt %. This is almost identical to the result obtained from inductively coupled plasma mass spectrometry (ICP-MS) (1:3.1).

The mesoporous structure of RhNi@NHMCs is further characterized to be a nearly two-dimensional (2D) *p6mm* from small-angle X-ray scattering (SAXS). After encapsulating RhNi alloys, the SAXS peaks are retained well, indicating the well-reserved mesostructures with the *d*-spacing size of 11.6 nm (Figure 2a). Meanwhile, the N₂ sorption isotherms of RhNi@ NHMCs exhibit a typical type IV loop, confirming the mesoporous structure of the sample (Figure 2b).^{48,49} The Brunauer–Emmett–Teller (BET) specific surface area is up to 1154 m² g⁻¹, with two distinct pore sizes of 6.8 and 2.9 nm (Figure 2c). This is a result of the RhNi alloys that occupy parts of mesoporous channels. The mesoporous framework thickness is thus estimated to be 4.8 nm (11.6–6.8), which is consistent with the data observed from the TEM and STEM images.

Wide-angle X-ray diffraction (XRD) was also studied for revealing the crystalline structure of the bimetallic RhNi alloys in RhNi@NHMCs. Four diffraction peaks appear in the region of 35–90°, suggesting that RhNi nanoclusters are compositionally well-alloyed with an fcc crystalline structure (Figure 2d). Meanwhile, the high-resolution X-ray photoelectron (XPS) Rh 3d spectra exhibit two pairs of signals assigned to Rh⁰ (major) and Rh³⁺ (minor) (Figure 2e). Compared to those in Rh@NHMCs (Figure S4), all of the peaks of XPS Rh 3d in RhNi@NHMCs slightly shift toward the lower binding energies. This implies the change in surface electronic states of Rh after alloying with Ni.^{33–35} Similarly, three pairs of XPS Ni 2p, which can be assigned to Ni⁰, Ni²⁺, and their satellites, are observed in RhNi@NHMCs, indicating a multielectron excitation process (Figure 2f).

The successful synthesis of ultrafine RhNi alloys encapsulated within the NHMCs provided a direct platform to evaluate their catalytic performance and further understand the corresponding catalytic mechanism of the room-temperature hydrolysis of AB. The catalytic performance of RhNi@ NHMCs for H₂ production from the hydrolysis of AB was evaluated at 25 °C (298 K). Meanwhile, monometallic Rh@ NHMCs and commercial Rh/C were also investigated for comparisons (see TEM in Figure S5). Obviously, RhNi@ NHMCs exhibited the best activity for the catalytic hydrolysis of AB with a complete H₂ production time of 2.0 min (Figure 3a). This corresponded to a superior turnover frequency (TOF) value of 1294 mol_{H₂} mol_{Rh}⁻¹ min⁻¹. By comparison, the hydrolysis times catalyzed by Rh@NHMCs and Rh/C prolonged to 2.8 and 32.0 min with the TOF values of 708



Figure 5. (a) Time-dependent plots of the produced H_2 over RhNi@NHMCs, Rh@NHMCs, and Rh/C under different test temperatures. (b) Relationships between In TOF and 1000/T and (c) calculated E_a values of RhNi@NHMCs, Rh@NHMCs, and Rh/C. The catalytic conditions are as follows: 20 mg of AB, 2.4 mg of catalysts, 7.0 mL of H_2O , and different test temperatures.

and 75 mol_{H₂} mol_{Rh}⁻¹ min⁻¹, respectively. Besides, all three catalysts produced ~42 mL of H₂ with an exact H₂/AB ratio of ~3.0, indicating that H atoms bonded with B in AB were totally hydrolyzed with 3 moles of H₂O. This also confirmed that all of the catalysts had nearly 100% H₂ selectivity for the catalytic hydrolysis of AB.¹¹ When further compared with Rh-based and other catalysts reported before (Tables S1 and S2),^{28,29,50–53} RhNi@NHMCs also represented the high active nanocatalyst for H₂ production from the room-temperature hydrolysis of AB (Figure 3b).

The compositional effect of binary RhNi alloys in RhNi@ NHMCs on the catalytic activity of the hydrolysis of AB is also investigated (see Figure S6 for TEM images). As shown in Figure 3c, with increasing Rh amounts, the catalytic activities dramatically increase and reach the top with an optimum Rh/ Ni of 1/3. Then, the catalytic activities slightly decrease with a further increase in Rh amounts. The volcano-like activities agree well with the previous reports in bimetallic nanocatalysts, confirming the importance of the compositional synergies of the catalysis.¹⁸ The catalytic stability of optimized RhNi@ NHMCs is further evaluated by consecutively injecting fresh AB into the previous solution. The rates of H₂ production only slightly decrease during the cycling tests with the complete H₂ production time of 3.5 min at five cycles (Figure 3d) because of the functional NHMC support that anchors and confines the RhNi alloys. In comparison, commercial Rh/C is quickly deactivated during cycling tests (Figure S7). These results coincide with the high efficiency of RhNi@NHMCs for the H₂ production from the hydrolysis of AB under ambient conditions (see Figure S8 for the TEM images after the stability tests).

The catalytic kinetics of RhNi@NHMCs for the hydrolysis of AB was thoroughly evaluated and further compared with Rh@NHMCs and commercial Rh/C. Figure 4a shows the time-dependent plots of the produced H_2 under different AB amounts catalyzed by RhNi@NHMCs, Rh@NHMCs, and

Rh/C. Impressively, the plots are completely overlapped in the initial stages for all three samples (<30 mL of H₂ produced). Meanwhile, their logarithmic plots of H_2 (ln TOF) and AB concentration (ln [AB]) are nearly horizontal, indicating zeroorder kinetics with respect to AB concentrations (Figure 4c).^{20,37} This rules out the cleavage of B-N and B-H bonds as the rate-determining step, when the above samples are used as catalysts. In contrast, the rates of H₂ production are obviously accelerated with the increasing catalyst (Rh) concentrations (Figure 4b). Their slopes of ln TOF and ln [Rh] are also calculated to be 1.09 for RhNi@NHMCs, 0.73 for Rh@NHMCs, and 0.83 for Rh/C (Figure 4d). This suggests that the hydrolysis of AB is a first-order reaction in the catalyst (Rh) concentrations.²⁰ Among them, RhNi@NHMCs hold a slightly higher slope (quicker catalysis), confirming the favorable hydrolysis for H₂ production.

The temperature effect of the above Rh-based catalysts in the hydrolysis of AB is further investigated. The hydrolysis of AB is dramatically accelerated with the increase in the test temperature from 293 to 313 K (Figure 5a). The relations between ln TOF and 1/1000 are also presented, which match well with the Arrhenius plots (Figure 5b). The activation energy (E_a) was further calculated based on the Arrhenius equation. Obviously, RhNi@NHMCs hold the lowest E_a value of 18.6 kJ mol⁻¹. By sharp comparison, the E_a values of Rh@ NHMCs and Rh/C are 38.6 and 61.5 kJ mol⁻¹, respectively (Figure 5c). The lowest E_a confirmed that, in comparison to Rh@NHMCs and Rh/C, RhNi@NHMCs have a thermodynamically lowest energy barrier and thus favorably accelerate the H₂ production from the hydrolysis of AB.^{20,54}

There are several catalytic mechanisms of the hydrolysis of AB over metal-based catalysts. Xu proposed that H_2O was first activated and further attacked and cleaved the B–N bond. Then, the hydrolysis of the cleaved NH_3 produced H_2 accordingly.⁵⁵ Jagirdar and Ma thought that H in B–H of NH_3 –BH₃ was cleaved in the attack of H_2O and adsorbed on

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Figure 6. (a) Time-dependent plots of the produced H_2 over RhNi@NHMCs in H_2O and D_2O . (b) Time-dependent plots of the produced H_2 over RhNi@NHMCs in different NaOH concentrations. (c) Proposed catalytic mechanism for the room-temperature hydrolysis of AB catalyzed by RhNi@NHMCs. The catalytic conditions in (a) are as follows: 20 mg of AB, 2.4 mg of catalysts, 7.0 mL of H_2O (or D_2O), and 25 °C. The catalytic conditions in (b) are as follows: 20 mg of catalysts, 7.0 mL of H_2O , different concentrations of NaOH, and 25 °C.

metal catalysts (*via* M–H bond). After that, another H_2O further attacked the M–H intermediate to produce H_2 .^{14,56} Besides, Fu proposed that NH_4^+ –BH₃(OH⁻) intermediate formed by the attacked H_2O was the key for H_2 production.⁵⁷ Very recently, Chen, Duan, and Austruc have highlighted that the oxidation cleavage of the O–H bond in the attacked H_2O was the rate-determining step for the H_2 production from the hydrolysis of AB, especially when catalyzed by noble-metal catalysts.^{16,18,58}

To unveil the catalytic mechanism for the room-temperature hydrolysis of AB over RhNi@NHMCs, more kinetic experiments were carefully designed and carried out. First, isotopic experiments with D₂O instead of H₂O as the solvent and reactant were performed for the catalytic hydrolysis of AB.^{18,59,60} As shown in Figure 6a, the hydrolysis rates were remarkably decelerated in the presence of D₂O, compared to H₂O. The kinetic isotope effect (KIE) was calculated to be 2.96, clearly confirming that the rate-determining step was the oxidation cleavage of the covalently stable O-H bond (rather than the cleavage of the B-N and B-H bonds in AB) when catalyzed by RhNi@NHMCs. Meanwhile, the role of OH⁻ was further investigated by conducting the hydrolysis reactions in different NaOH concentrations (Figure 6b).^{20,61} Interestingly, the hydrolysis activities were remarkably enhanced with the increasing NaOH concentrations and reached the top value at 0.5 M NaOH with a very high TOF value of 2589 mol_H, $mol_{Rh}^{-1} min^{-1}$ (Figure S9). This TOF value in 0.5 M NaOH was 2.0 times higher than that without NaOH. This indicates that OH⁻ can be favorably coordinated on the catalyst and result in a more electron-rich surface, which would benefit the rate-limiting oxidation coordination of H2O. However, the hydrolysis activities became slightly worse in the higher NaOH concentrations, since excessive OH⁻ could cover the catalytic sites for the oxidation cleavage of the O-H bond.¹⁸

According to the above discussions, we ascribe the higher activity of RhNi@NHMCs to their multiple compositional and structural synergies that kinetically accelerate the oxidation cleavage of the covalently stable O-H bond in the attacked H_2O (the rate-determining step) and accordingly promote the

catalytic hydrolysis of AB under ambient conditions (Figure 6c). On one hand, alloying more oxophilic Ni with Rh would introduce new surface functions that favor the coordination of H_2O on the Ni surface (via $H_3N-BH_2-H\cdots H-OH$) and thus facilitate the oxidation cleavage of the O-H bond in the attacked H_2O (functional effect). On the other hand, alloying Ni could modify the surface electronic structure of Rh and thermodynamically lower the E_{a} on the Rh surface (electronic effect). This directly accelerates the oxidation cleavage of the O-H bond in the attacked H₂O. Meanwhile, spatially separated catalytic sites of Rh and Ni in an optimum compositional ratio (1/3) synergistically accelerate the cleavage of H₂O for H₂ production. Furthermore, hierarchical hollow and mesoporous nanospheres are able to kinetically facilitate electron/mass transport in the reaction solution, while N-functionalized surface on NHMCs partially optimizes the coordination of H₂O on the supports. They also cause improved coordination of H₂O on the catalyst surface, therefore kinetically promoting the H₂ production from the hydrolysis of AB.

CONCLUSIONS

We report an effective self-limiting method to grow in situ supported ultrafine bimetallic RhNi nanocatalysts on Nfunctionalized HMCs and demonstrate their high efficiency for H₂ production from the room-temperature hydrolysis of AB. The obtained RhNi@NHMCs hold a very high TOF value of 1294 $\text{mol}_{\text{H}_2} \text{ mol}_{\text{Rh}}^{-1} \text{ min}^{-1}$ and a low E_{a} value of 18.6 kJ mol⁻¹, representing the top level ever developed for alternative noble-metal catalysts. Detailed kinetics investigations, including D₂O replacement and NaOH-promotion experiments, reveal that, when catalyzed by RhNi@NHMCs, the ratedetermining step is the oxidation cleavage of the covalently stable O-H bond, rather than the cleavage of the B-N and B-H bonds. Compositional and structural advantages of RhNi@NHMCs result in multiple functional, electronic, and support synergies for the hydrolysis of AB. We demonstrate that functional and electronic effects of bimetallic RhNi alloys facilitate the coordination of H₂O and accelerate the oxidation

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cleavage of the O–H bond in the attacked H_2O , while a hierarchical HMC support optimizes the electron/mass transport during the hydrolysis of AB. The utilization of the supported Rh-based alloys to fabricate highly active catalytic sites might be easily extended to other metal alloy catalyst systems with defined functional and electronic synergies for various targeted catalytic reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00721.

Details of the synthesis, characterizations, and catalytic measurements and more SEM and TEM images as well as the evaluation of catalytic performances (PDF)

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Notes

The authors declare no competing financial interest.

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