Facile Fabrication of Rhodium/Nanodiamond Hybrid as Advanced Catalyst toward Hydrogen Production from Ammonia–Borane

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Abstract: Hydrogen generation through ammonia–borane (AB) hydrolysis has been regarded as one of the most promising pathways to tap renewable green energy. The design and synthesis of highly effective catalysts toward hydrogen production from aqueous AB is of paramount significance. Here, the facile synthesis of Rh nanoparticles (NPs) immobilized on nanodiamond (nano-DA) and concomitant AB hydrolysis to produce hydrogen was successfully achieved. The in situ generated Rh/nano-DA exhibited excellent catalytic activity toward AB hydrolysis, with a high turnover frequency (TOF) value of 729.4 min$^{-1}$ at 25 °C and a low activation energy of 25.6 kJ mol$^{-1}$. Moreover, the catalyst could be reused four times. The unique properties of DA with abundant oxygen-containing groups enable the homogeneous distribution of small and surface-clean Rh NPs on the nano-DA surface, which can supply abundant accessible active sites for hydrogen evolution from AB hydrolysis. This study demonstrated that nano-DA can be applied as an ideal matrix to deposit efficient Rh nanocatalyst toward hydrogen evolution reaction.

Keywords: nanodiamond; ammonia–borane; hydrogen evolution; rhodium nanoparticles

1. Introduction

Hydrogen is regarded as a clean fuel by virtue of its environmental friendliness, high density, and high energy content [1–3]. However, the lack of efficient strategies in the storage and release of hydrogen considerably restricts the large-scale applications. Recently, hydrogen release from hydrogen storage materials, including metal hydrides, chemical hydrides, and sorbent materials, has sparked increasing interest [4–7]. Typically, ammonia–borane (AB) has been considered a promising hydrogen source due to its featured merits of high hydrogen capacity (19.6 wt%), high stability in the solution, and non-toxicity under ambient conditions [8–11]. Compared with thermal treatment, hydrogen evolution from AB hydrolysis can be achieved under ambient conditions with a suitable catalyst, with the generation of three equivalents of hydrogen per mol AB (Equation (1)) [12,13]. The design and synthesis of efficient catalysts that can considerably promote the hydrogen generation rate for AB hydrolysis is critical:

\[ \text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^{2-} + 3\text{H}_2\text{O} \] (1)

Noble metals (Rh, Ru, Pt, etc.) have shown remarkable hydrogen production efficiency [14–17]. Notably, Rh is among the most extensively investigated catalysts for hydrogen generation from AB hydrolysis owing to its intrinsic catalytic performance toward the reaction [17–22]. It is well known that catalyst support can significantly affect catalytic activity via controlling the growth and dispersion of metal nanoparticles (NPs) in the synthetic process. The materials with plenty of functional groups of oxygen-containing groups, such as SiO$_2$ [23], TiO$_2$ [24,25], and CeO$_2$ [18], have been developed for the
synthesis of catalysts in the hydrolysis of AB. However, Rh NPs deposited on those supports exhibited unsatisfied catalytic activity with relatively low turnover frequency (TOF) values except for CeO$_2$. Despite the presence of oxygen-containing groups in conventional supports, the metal NPs deposited on these supports are easily agglomerated to large particles because of the relatively low interaction between metal and supports, which provides insufficient stabilization for the metal NPs [26]. Owing to the specific pore structure and abundant surface functional groups, two dimensional graphene is also investigated as support to immobilize metal Rh NPs for AB hydrolysis [27]. Nevertheless, the present catalytic system still suffers from the drawbacks of complicated synthetic procedure and relatively low catalytic activity. Therefore, it is essential to develop catalyst support that can effectively anchor metal NPs affording a tremendous number of active sites for AB hydrolysis.

Recently, nanodiamond (nano-DA) has received increasing attention due to the featured advantages of excellent thermal conductivity and chemical inertness [28]. Thus, nano-DA has been exploited as catalyst for organic oxidation and electrocatalysis [29,30]. Unfortunately, no report is available on the synthesis of nano-DA-stabilized Rh NPs for AB hydrolysis to hydrogen evolution. Here, we reported the in situ synthesis of Rh NPs on nano-DA and the concomitant hydrogen generation from AB hydrolysis under mild conditions. The results showed that Rh/nano-DA could be used as an effective catalyst toward AB hydrolysis to produce hydrogen at room temperature without any additives. Specially, the Rh/nano-DA catalyst delivered a high turnover frequency (TOF) of 729.4 min$^{-1}$, which was higher than that of most previously reported Rh-based catalysts. Meanwhile, the catalyst could be recycled at least four times. The present study demonstrates that the nano-DA is an excellent matrix for synthesizing an efficient catalyst in the hydrolysis of AB.

2. Results

Figure 1a,b show the TEM images of Rh/nano-DA with an optimal Rh loading of 3.1 wt%. The in situ formed Rh NPs are well distributed on the nano-DA surface with an average size of 3.0 nm (Figure 1c). The high-resolution TEM (HRTEM) image revealed the distinct lattice fringes with a d-spacing of 0.206 nm corresponding to the (220) plane of nano-DA (Figure 1a inset) [31,32]. Moreover, the HRETM image also exhibited the clear lattice fringe with an interplanar spacing of 0.21 nm consistent with the Rh (111) plane (Figure 1b inset) [33]. It should be pointed out that particle size of Rh NPs is expected to be gradually increased because of the possible NP agglomeration with increasing loading of Rh, which are normally observed from supported metal NPs [34]. This can be verified by the typical TEM image of Rh/nano-DA with a Rh loading of 3.77 wt%, in which a large particle size of 3.43 nm was observed (Figure S1). Figure 1d exhibits the XRD pattern of Rh/nano-DA. The two sharp and strong diffraction peaks at 43.9° and 75.6° belonged to the reflection (111) and (220) planes of nano-DA. There were no obvious peaks of Rh or Rh oxide species detected in the XRD pattern due to the small-sized and uniform dispersion of Rh, providing the best agreement with the TEM results. Figure 1e depicts the FTIR spectra of nano-DA and Rh/nano-DA. The peaks at 3296 and 1774 cm$^{-1}$ were attributed to the stretching vibrations of O–H and C=O groups, suggesting the presence of carbonyl and hydroxyl groups on the surface of pristine nano-DA [35]. Compared with pristine nano-DA, no considerable changes were observed in the FTIR spectrum of Rh/nano-DA, showing that the frame structure of pristine nano-DA was not affected after Rh loading. Compared with the pure nano-DA, the spectrum of Rh/nano-DA spectra demonstrates more distinct and sharp bands that could be related to the interplay active phase on the surface support and the metal–carbon interactions [36]. N$_2$ adsorption–desorption isotherms were recorded to determine the surface area of nano-DA and Rh/nano-DA. According to Brunauer–Emmett–Teller (BET) analysis, the BET surface area of nano-DA was calculated to be 300.3 m$^2$ g$^{-1}$, while the BET surface area of Rh/nano-DA decreased to 210.0 m$^2$ g$^{-1}$ because of the block of nanopores by Rh NPs [37].
The surface composition and the elementary chemical states of Rh/nano-DA were further studied by XPS. Figure 2a shows the XPS survey scan of Rh/nano-DA, from which the C, O and Rh elements are distinctively observed. To study the chemical states of the detected elements, high-resolution XPS spectra of Rh3d, C1s, and O1s were recorded. The Rh 3d core level spectrum displayed in Figure 2b demonstrated two contributions at 307.1 and 311.8 eV, which could be ascribed to Rh$^0$ [38–40]. Regarding the C1s spectrum, the deconvoluted peaks at 283.5, 284.8, 286.1 eV could be assigned to the C–C, C=C and C–OH, respectively (Figure 2c) [41,42]. The O 1s spectrum illustrated in Figure 2d displayed two fitted peaks at 529.9 and 531.2 eV, which could be ascribed to Rh–O and C–OH [33,43,44]. The aforementioned results confirm the successful synthesis of Rh/nano-DA with small Rh NPs and the abundant surface-oxygen-containing groups. It is expected that the small Rh NPs can supply more surface-active sites for AB hydrolysis and the hydrophilicity of Rh/nano-DA originated from the abundant surface-oxygen-containing groups are beneficial for the dispersion of the catalyst in the aqueous phase, reducing the mass transportation during the reaction.
Figure 2. (a) XPS full spectrum of Rh/nano-DA. High-resolution XPS spectra of (b) Rh 3d; (c) C 1s; (d) O 1s.

Hydrogen generation from AB hydrolysis was utilized as a model reaction to explore the catalytic activity of Rh/nano-DA. The control experiment using nano-DA showed negligible hydrogen release, whereas large amounts of hydrogen gas was released with the aid of Rh/nano-DA. This observation indicated that the catalytically active sites for AB hydrolysis were Rh species rather than nano-DA.

To study the rate law of AB hydrolysis catalyzed by Rh/nano-DA, the hydrolysis reaction was performed at 25 °C with varied Rh contents (i.e., 0.29, 0.58, 0.87, and 1.16 mM). Figure 3a shows the results of hydrogen production against the reaction time with different Rh contents. With the increasing Rh content, the hydrogen generation rate (HGR) increased accordingly. To compare the corresponding catalytic activity, the TOF values of Rh/nano-DA with different Rh contents were calculated. The Rh/nano-DA with the Rh content of 0.87 mM could catalyze AB hydrolysis to yield the highest TOF value of 673.3 min⁻¹, which was higher than the catalysts with Rh contents of 0.29, 0.58, and 1.16 mM with TOFs of 508.9, 572.3 and 562.2 min⁻¹, respectively. The HGRs for the Rh/nano-DA catalysts with different Rh contents were determined according to the slopes of the fitting lines from the first five time increments at different Rh concentrations. The logarithmic plots of HGR vs. Rh concentration were displayed in Figure 3b. The corresponding slope of the fitting line was calculated to be 0.53, indicating a different reaction mechanism for AB hydrolysis catalyzed by Rh/nano-DA in comparison with the reported results where quasi-first-order or quasi-zero-order kinetics were proposed [45,46]. Hence, the catalyst Rh/nano-DA with 0.87 mM of Rh concentration was chosen for further investigation.
Table 1. Herein, the low $E_a$ value is probably ascribed to the structural features of Rh NPs and nano-DA matrix. As a result, Rh/nano-DA is highly active for AB hydrolysis:

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Figure 3c shows the plots of hydrogen generation from AB dehydrogenation at different substrate concentrations in the range of 150–300 mM. The TOF values of Rh/nano-DA with different AB concentrations were calculated. The maximum TOF value of 729.4 min$^{-1}$ was observed with the AB concentration of 150 mM, whereas lower TOFs of 673.3, 527.4, and 476.1 min$^{-1}$ were observed with AB concentrations of 200, 250, and 300 mM. The HGRs were determined according to the slopes of the fitting lines from the first five time increments at different AB concentrations. The logarithmic plots of the HGR vs. AB concentration were constructed and the results are shown in Figure 3d. It was found that the HGR for AB hydrolysis was dependent of AB concentrations. As a demonstration, a straight line with a slope of -1.06 was observed via fitting the logarithmic plot of HGR vs. AB concentration. This observation indicated that AB hydrolysis catalyzed by Rh/nano-DA was a first-order reaction in terms of substrate concentration.

Reaction temperature is an essential factor that affects the rate of hydrogen generation from AB hydrolysis. Therefore, AB hydrolysis over Rh/nano-DA was conducted at varied temperatures from 25 to 40 °C. The values of the rate constant $k$ at different temperatures for AB hydrolysis with Rh/nano-DA were obtained by fitting the first five time increments at different AB concentrations. The HGR for AB hydrolysis increased with the elevation of reaction temperature, indicating the vital role of the reaction temperature in improving the catalytic activity of Rh/nano-DA. As a critical kinetic parameter, the activation energy ($E_a$) for Rh/nano-DA-catalyzed AB hydrolysis can be calculated on the basis of the Arrhenius equation (2) and the related Arrhenius plot (Figure 3f) [47,48]. Accordingly, the $E_a$ is determined to be 25.6 ± 1.0 kJ mol$^{-1}$, which was lower than many previous results as shown in Table 1. Herein, the low $E_a$ value is probably ascribed to the structural features of Rh NPs and nano-DA matrix. On the one hand, Rh NPs were evenly distributed on the surface of nano-DA matrix, providing highly dispersed active sites [3,6,49]. On the other hand, a nano-DA matrix with abundant oxygenated
functional groups can efficiently stabilize the Rh NPs and impede their agglomeration [50]. As a result, Rh/nano-DA is highly active for AB hydrolysis:

$$\ln k = \frac{E_a}{RT} + \ln A$$  \hspace{1cm} (2)

**Table 1.** Comparison results with the reported Rh-based catalysts toward AB hydrolysis.

| Catalysts               | Temperature (°C) | Metal/AB (mol/mol) | TOF (Turnover Frequency) (min⁻¹) | $E_a$ (kJ mol⁻¹) | Refs. |
|-------------------------|------------------|--------------------|----------------------------------|-----------------|-------|
| In situ Rh/C             | 25               | 0.004              | 1246                             | 40.9            | [15]  |
| Rh₀/ CeO₂               | 25               | 0.0008             | 2010                             | 42.6            | [18]  |
| Rh/PPC                  | 25               | 0.005              | 806                              | 22.7            | [19]  |
| HCP-PPh₃-Rh             | 25               | 0.002              | 481                              | 23.8            | [8]   |
| Rh/Carbon-SC            | 25               | 0.003              | 336                              | 37.1            | [51]  |
| Rh/graphene             | 25               | 0.04               | 325                              | 19.7            | [27]  |
| Rh/γ-Al₂O₃              | 25               | 0.018              | 128.2                            | 21.0            | [52]  |
| Rh(0)/TiO₂              | 25               | 0.00116            | 260                              | 65.5            | [24]  |
| Rh/ nanoZrO₂            | 25               | 0.02               | 198                              | 48              | [53]  |
| Ru-Rh@PVP               | 25               | 0.003              | 386                              | 47.4            | [54]  |
| Rh/AC                   | 25               | 0.0009             | 180                              | 39.9            | [55]  |
| Rh/PCNs                 | 25               | 0.004              | 513.2                            | 46.5            | [56]  |
| Rh/g-C₃N₄               | 25               | 0.003              | 969                              | 24.2            | [57]  |
| Rh₀/nanoSiO₂            | 25               | 0.0008             | 112                              | -               | [18]  |
| Rh₀/nanoAl₂O₃           | 25               | 0.0008             | 112                              | -               | [18]  |
| Rh₀/HfO₂                | 25               | 0.0008             | 24                               | -               | [18]  |
| Rh(0)/CNT               | 25               | 0.0025             | 706                              | 32              | [58]  |
| Zeolite stabilized Rh(0) | 25              | 0.002              | 92                               | 66.9            | [20]  |
| Laurate stabilized Rh(0) | 25              | 0.0025             | 200                              | 43.6            | [21]  |
| Rh/nano-DA              | 25               | 0.006              | 729.4                            | 25.6            | This work |

The reusability of a heterogenous catalyst is a key criterion in terms of practical application. To investigate the reusability of a Rh/nano-DA catalyst for AB hydrolysis, the used catalyst was recovered from the mixture after the previous run was completed. The recycling tests were performed four times and the results are shown in Figure 4a. It was observed that the Rh/nano-DA catalyst could catalyze AB hydrolysis after four recycling runs with the generation of three equivalents of H₂ per mole of AB. The time for the complete conversion of AB increased with the increasing recycling runs. The TOF value of each recycling run was calculated and the results are shown in Figure 4b. Note that the Rh/nano-DA catalyst still possessed 42.2% of the initial catalytic activity for the hydrolysis of AB. The catalytic activity loss of Rh/nano-DA during the recycling tests was further discussed. The reused catalyst was further characterized by TEM and the results are shown in Figure 4c,d. It was found that the aggregation of Rh NPs occurred during the recycling process and the size of Rh NPs increased to 4.0 nm (Figure 4c inset), which was responsible for the loss of catalytic activity. However, it should be pointed out that the present strategy for hydrogen evolution from aqueous AB avoids the tedious catalyst reduction and washing steps, which is economic and environmentally friendly. Indeed, the reusability of Rh/nano-DA for AB hydrolysis toward hydrogen evolution must be further improved.
Figure 4. (a) Plots of hydrogen generation for different recycling runs; (b) the retained activity of each cycle; (c, d) TEM images of recycled catalyst (inset is corresponding size distribution).

3. Discussion

Notably, the TOF value of 729.4 min\(^{-1}\) for Rh/nano-DA was superior to that of many reported catalysts in Table 1. The high performance of Rh/nano-DA for AB hydrolysis was further discussed. First, it is generally accepted that small metal NPs of supported catalysts can supply an abundance of surface-active sites and thereby induce a high catalytic activity toward catalytic applications. The small Rh NPs with a diameter of 3.0 nm are expected to have a high dispersion on the support surface and more surface catalytically active atoms are provided for AB hydrolysis. Second, the presence of abundant surface-oxygenated groups on nano-DA are beneficial for the affinity of an Rh precursor and the resulting Rh NPs on the surface of DA, which can maintain the catalytic activity of Rh/nano-DA during the hydrolysis reaction. Finally, the high hydrophilicity of Rh/nano-DA enables itself to uniformly disperse in aqueous solution, reduce the mass transfer and benefit the interaction between substrate and active sites. Hence, the catalytic hydrolysis of AB catalyzed by Rh/nano-DA was greatly accelerated.

Compared with previously reported results, present study has the following featured advantages: (a) the in situ generation of Rh NPs on the nano-DA and concomitant hydrolysis were achieved by a one-pot method, which avoids the tedious catalytic preparation procedures, such as the reduction, washing and drying steps, enabling the whole process to be simple, cost-effective and energy-saving; (b) the achieved Rh/nano-DA delivered a very high catalytic activity of 729.4 min\(^{-1}\), which was higher than most of the reported Rh-based catalysts toward hydrogen generation from AB hydrolysis;
and (c) the catalyst was reusable and could be recycled at least for four times. Nevertheless, the reusability of the present catalyst was not sufficiently satisfied. Further work should be done to improve the reusability of Rh/nano-DA for AB hydrolysis.

4. Materials and Methods

4.1. Chemicals

RhCl$_3$·nH$_2$O was purchased from Kunming Institute of Precious Metals (Kunming, China). Nano-DA was obtained from Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China). Ethanol was supplied by Aladdin-reagent Inc. (Shanghai, China) and ammonia–borane (AB) complex (90%) was purchased from Aldrich (Shanghai, China). All chemicals were used as received without any purification. The deionized water (DI water, 18.2 MΩ) was used in all experiments.

4.2. Preparation of Rh/nano-DA and Concomitant AB Hydrolysis

Briefly, 8.3 mg RhCl$_3$·nH$_2$O was added to 20 mL ethanol and followed by ultrasonication for 30 min. Afterward, 100 mg nano-DA was transferred into the RhCl$_3$ ethanol solution. The achieved suspension was stirred at 60 °C for 2 h. Then, the solvent was evaporated and the resulting powder was further dried at 100 °C before use. The Rh loading of Rh/nano-DA was 3.1 wt%, determined by inductively coupled plasma optical emission spectrometry (ICP–OES). For comparison, the Rh/nano-DA samples with different Rh loading were prepared in the same procedures except for changing the weight of RhCl$_3$·nH$_2$O. The accurate Rh loading of each sample was determined by ICP–OES.

The hydrogen evolution reaction for AB hydrolysis with Rh/nano-DA was conducted as follows. In a typical procedure, 15 mg Rh/nano-DA and 4 mL deionized water were mixed via ultrasonication for 0.5 h to obtain a homogenous suspension at room temperature. Then, the dissolved AB solution (1 mL, 150 mM) was quickly injected into the reactor to trigger the hydrolysis reaction. The generated hydrogen was recorded by water displacement method. To ensure the reproducibility, the amounts of nano-DA and RhCl$_3$·nH$_2$O were accurately weighed and the synthetic conditions were strictly controlled under the same conditions. The hydrolysis reaction over Rh/nano-DA was repeatedly tested three times. The corresponding results showed that the catalytic activity of Rh/nano-DA has good reproducibility.

For the stability test, the catalyst was collected by centrifugation and then rinsed with deionized water. The separated solid was reused to catalyze the next run for AB hydrolysis by adding fresh AB solution.

4.3. Characterization

The morphology of Rh/nano-DA was characterized by Transmission electron microscopy (TEM) with a JEM-2100F equipment (JEOL, Akishima City, Japan) under 200 kV. The crystal structure of the sample was recorded by powder X-ray diffraction (XRD) on a Panalytical X’Pert diffractometer (Tokyo, Japan) with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Thermo ESCALAB 250 Axis Ultra spectrometer (Waltham, MA, USA). The Fourier transform infrared spectroscopy (FTIR) spectrum was performed on NEXUS 670 (Thermo Nicolet, Waltham, MA, USA) infrared spectrophotometer. ICP–OES was performed on a SPECTRO ARCOS spectrometer equipment (Kleve, Germany).

5. Conclusions

In summary, Rh NPs with a diameter of 3.0 nm were in situ synthesized and supported on the nano-DA surface by utilizing rhodium (III) chloride as the metal precursor and ammonia–borane as the reactant and a reducing agent in aqueous solution. The in situ formed Rh/nano-DA was simultaneously acted as an efficient catalyst toward AB hydrolysis. The Rh/nano-DA catalyst showed a high TOF value of 729.4 min$^{-1}$ together with $E_a$ value of 25.6 kJ mol$^{-1}$, which were better than many of the reported
Rh-based catalysts. The high catalytic performance could be attributed to the high hydrophilicity of the support nano-DA and the well dispersion of small Rh nanoparticles, which can reduce the mass transportation and provide abundant catalytically active sites for AB hydrolysis. This work shows that nano-DA can be used to prepare other nano-DA-stabilized NPs as catalysts for other important applications.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/9/1037/s1, (a) TEM image and (b) Rh size distribution of Rh/nano-DA with Rh loading of 3.77 wt%.

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