Hollow Mesoporous Silica Supported Ruthenium Nanoparticles: A Highly Active and Reusable Catalyst for H₂ Generation from the Hydrolysis of NaBH₄

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1. Introduction

Renewable energy has attracted much attention because of the ever-growing demands in energy conservation and friendly environmental protection. Moreover, an increasing number of personal electronic products also require efficient energy resources for on-board energy generation [1]. The proton-exchange membrane fuel cell (PEMFC) is thought to be the most promising fuel cell type for commercialization in future because of the high performance at low temperatures [2]. However, a safe, high-purity, and efficient H₂ production and storage have become a major concern for a PEMFC system [3]. So far, increasing attention has been paid on on-board H₂ production method, and a number of significant outcomes have been achieved [4]. Among various H₂ storage systems, chemical hydrides are widely used as candidates of hydrogen generation in terms of the portable application due to the obvious advantages, such as high H₂ capacity, well storability and controllability, low reaction-initiating temperature, and environmentally benign by-product [5].

The alkaline NaBH₄ solution (pH > 13) is very stable only if specific catalysts are contacted. Until now, many transition metals and alloys have been found effective in accelerating NaBH₄ hydrolysis [6–12]. Despite that fact that nonnoble catalysts have a cost advantage, precious metal catalysts demonstrate significantly higher catalytic activities than an equivalent amount of nonnoble catalysts [13]. To build highly efficient catalysts for NaBH₄ hydrolysis, the Ru-based heterogeneous catalysts still remain the preferred choice due to its price advantage among the other precious metals, such as Pt and Pd.

The activity of heterogeneous catalysts is greatly influenced by the interfaces between supporters and metal nanoparticles. To date, the most reported supports for the hydrolysis of NaBH₄ are mainly focused on conventional supports, like aluminum oxide (Al₂O₃), activated carbon (C), and ion-exchange resins, and so forth. Nevertheless, some ordered-structure supports, such as layered materials and mesoporous materials, have received few attention in the field.
of the hydrolysis of NaBH₄. From our recent work, Ru nanoparticles have been successfully deposited on the external surface of montmorillonite, which greatly improved the catalytic activity due to the surface of the Ru nanoparticles (MMT) exposed. But we also found that the residual activity of the reused catalyst deteriorated, which was attributed to the aggregation and partial fall-off of the deposited Ru nanoparticles [14]. The better solution builds a more robust heterogeneous catalyst.

Because hollow mesoporous silica with available interior cavity and highly permeable mesoporous shell is convenient for the loading of different kinds of guest species, it has been widely utilized in many different fields, such as confined preparation and catalysis [15]. In view of more abundant functional groups in HMS surface than MMT, a more robust catalyst is expected to stabilize Ru nanoparticles and favor recycling nanoparticles than MMT. In our present study, hollow mesoporous silica (HMS) was used to construct Ru-based heterogeneous catalyst (Ru/HMS). And the catalytic activity and reusability of the Ru/HMS nanocatalyst were determined for H₂ evolution from the hydrolysis of an alkaline NaBH₄ solution. In addition, the surface morphology as well as chemistry of the reused Ru/HMS catalyst was also investigated and discussed. The effects of NaBH₄ and catalyst concentrations on rate of H₂ generation in low temperature were summarized in this report. Moreover, the relation of activation energy versus catalyst concentration on hydrogen production from the hydrolysis reaction was discussed in detail to optimize the catalyst amount.

2. Experimental Section

2.1. Chemicals and Materials. Ruthenium chloride hydrate (RuCl₃ · xH₂O, Ru content ≥37%) was purchased from Sigma-Aldrich. NaBH₄, NaOH, and other used reagents were supplied from Sinopharm Chemical Reagent Co., Ltd. And all these chemicals are of analytical grade and used as received without further purification. Deionized water was obtained from a water purification system in our lab. Hollow mesoporous silica (HMS) was prepared according to the literature [16].

2.2. Preparation of Ru/HMS Catalyst. The Ru/HMS catalysts with different Ru loadings were prepared by in situ wet chemical reduction with NaBH₄ as the reducing agent. In a typical experiment, 2.5 g of HMS was dispersed into 200 mL of an aqueous RuCl₃ solution of desired concentration (1 wt%, 2 wt%, and 4 wt% of Ru with respect to HMS weight) and then mixed thoroughly by magnetic stirring at ambient temperature for 5 h to obtain Ru₃7/HMS, followed by the addition of an overdose of NaBH₄ (0.1 g) as a reducing reagent. The slurry rapidly turned into a grayish black dispersion and then was continued to stir vigorously for 1 h. Finally, catalyst powder was collected by washing using abundant deionized water to detach the other excess salt. The obtained samples were dried at 110°C for 10 h and then ground thoroughly in an agate mortar for further use.

2.3. Characterizations of Ru/HMS Catalyst. X-ray diffraction (XRD) patterns were examined using a Rigaku D/MAX-2200 diffraction using Ni-filtered Cu Kα radiation. The morphologies of the as-prepared and reused catalysts were carried out by a JEOL JSM-200CX transmission electron microscope (TEM) coupled with an energy-dispersive X-ray spectrometer (EDX). The electronic state of the surface elements was obtained from the X-ray photoelectron spectroscopy (XPS) measurement, which was performed on a VG Scientific ESCALAB 200 A spectrometer.

2.4. Evaluation of Catalytic Performance. The evaluation of the catalytic performance of the as-prepared and reused catalysts was determined by measuring the volume of H₂ evolved from the hydrolysis reaction by using a water-displacement method, which has been described in detail in our previous work [14]. During measurement, the temperature of catalytic system was monitored and carefully controlled within ±0.5°C by a thermostat.

To obtain the relationship of Ru/HMS catalyst and NaBH₄ concentrations on the rate of H₂ evolution from the hydrolysis of alkaline NaBH₄ catalyzed by the as-prepared Ru/HMS catalyst, the NaBH₄ hydrolysis was firstly performed with different catalyst amounts (10, 20, 40, and 80 mg) while keeping NaBH₄ (1 wt%) and NaOH concentration (3 wt%) constant; and then varying the concentration of NaBH₄ (1, 2.5, 5, and 10 wt%) when catalyst amount (10 mg) and NaOH concentration (3 wt%) are kept constant. To obtain the optimum value, the relationship of E₀ value versus catalyst amount is determined. The different catalyst amounts, that is, 10, 20, 40, and 80 mg, are used to catalyze NaBH₄ hydrolysis under constant NaBH₄ (1 wt%) and NaOH (3 wt%) under different temperatures ranged from 10°C to 30°C, respectively.

3. Results and Discussion

3.1. Characterization of Ru/HMS Catalyst. The aim of this investigation is to develop a facile and efficient method for preparing Ru/HMS nanocomposites as catalyst for the H₂ production from an alkaline NaBH₄ solution. Figure 1 shows the XRD patterns of the pristine HMS and Ru/HMS samples with different loadings in the small-angle range. As indicated in Figure 1(a), the pattern gives three well-resolved Bragg diffraction peaks, which can be attributed to the (100), (110), and (200) reflections of a hexagonal symmetry structure typical for MCM-41. The result is in accordance with those of the reported data [16], indicating the successful preparation of HMS. After being loaded with Ru nanoparticles, the Bragg diffraction intensities of these samples (Ru/HMS) become weaker compared with those of the pristine HMS; and with the Ru loading increasing, the intensity of the Bragg diffraction decreases. XRD results indicate that Ru nanoparticles have been successfully loaded in HMS, and the mesoporous structure of HMS is still remaining after being loaded with Ru nanoparticles.

The existence of Ru nanoclusters in HMS is further investigated by TEM measurements. Figure 2(a) shows a typical TEM image of the as-prepared Ru/HMS nanocomposites. As observed in the figure, sphere morphology with the size of
2-3 μm or so is clearly observed. And there is an obvious contrast between the core and the shell of the Ru/HMS sphere in the micrograph. The result of TEM image further proved that the synthesized HMS sphere has a hollow structure, which is in accordance with the reference. Further observed from the TEM micrograph with greater enlargement of Ru/HMS sample (Figure 2(b)), the thickness of the shells can be estimated in the range of 100–200 nm. The TEM image of the loaded Ru particles in the hollow region (Figure 2(c)) demonstrates many dark nanoparticles, and these particles should be assigned to be Ru nanoparticles, which is proved by the EDX result (Figure 2(f)). As indicated in the figure, the elemental Ru clearly exists in the catalyst sample. Furthermore, broad rings are shown in the electron diffraction (ED) pattern of the as-prepared Ru/HMS sample (Figure 2(e)), implying the nanocrystalline phase is formed. According to the diffraction rings, the d-spacings could be calculated to be 1.93 and 1.21 Å, which corresponds to the reflections of the (101) and (103) lattice planes of hexagonal close packed metal Ru, respectively [17]. As observed from the size distribution of the loaded Ru nanoparticles in Figure 2(d), the deposited particle size ranged from 10 nm to 42 nm, with a mean value of 23.4 nm. TEM results further prove that Ru nanoparticles have been successfully loaded in HMS, which is accordance with the result of XRD.

XPS measurements are used to further determine whether metallic Ru(0) nanostructures have been formed in Ru/HMS samples. The results are shown in Figure 3. From the survey spectrum (Figure 3(a)), the binding energies at 489.1 and 468.1 eV can be assigned to the characteristic peaks of Ru 3p1/2 and Ru 3p3/2, respectively; and the peak at 289.1 eV is ascribed to the characteristic peak of Ru 3d [18], further conforming the formation of metallic Ru(0) by in situ wet chemical reduction. Additionally, there exists Ru-O component in the high-resolution XPS at the Ru 3d except Ru⁰ in Ru/HMS catalyst (Figure 3(b)), which is probably due to the partial oxidation of the loaded Ru nanoclusters upon exposure to air at ambient temperature. Based on the XPS quantitative analysis, the experimental amount of Ru loaded in the HMS is calculated as 2.3 wt%, which is close to 2 wt%, the theoretical amount of Ru in HMS.

3.2. Evaluation of Catalytic Activity

3.2.1. Effect of Ru Loading. The plot of time-dependent H₂ generation from an alkaline NaBH₄ solution catalyzed by Ru/HMS with different loadings is shown in Figure 4. With HMS, nearly no H₂ generation produced. However, in the presence of Ru/HMS catalyst, the hydrolysis reaction immediately starts upon contact of the catalyst with the NaBH₄ solution. In addition, the linear increase in H₂ generation enables a continuable and controllable H₂ generation process for practical applications. Upon reaching a certain time, H₂ generation stops. The total H₂ yield reached 99% of the theoretically expected value. The catalytic performance is expected to depend on Ru loadings of Ru/HMS sample. Accordingly, the catalytic activity of Ru/HMS samples (in all the same amount of catalyst) with different Ru loadings in Ru/HMS was tested in the hydrolysis of alkaline NaBH₄ solution to determine the effect of Ru loading on the catalytic activity. As indicated in Figure 4(b), the rate of H₂ generation is the greatest when the Ru loading in Ru/HMS is 2.3 wt%. As the Ru loading increases, perhaps some of the Ru nanoclusters become larger, blocking the entrance to the interior cavity [19].

As displayed in Figure 4(a), H₂ can be totally released within 1200 s in the hydrolysis system with 40 mg of Ru/HMS loaded with 2.3 wt% Ru (Ru/NaBH₄ molar ratio = 0.003), and an average rate of H₂ generation reaches 18600 ± 500 mL · min⁻¹ · g(Ru)⁻¹ at 25 °C. The H₂ generation rate of Ru/HMS catalyst is lower than our previously reported value of Ru/MMT, which might be due to the confinement of the mesoporous shell of HMS. But the catalytic activity of Ru/HMS is still higher than those of most Ru-based heterogeneous catalysts used in the same catalytic system, like Ru/IRA-120, Ru/carbon, Ru/zeolite-Y, and so forth indicating that Ru/HMS is a high-efficiency catalyst for NaBH₄ hydrolysis. Accordingly, the sample with a 2.3 wt% Ru loading is used in the followed experiments for the further investigation.

3.2.2. Rate Equation of NaBH₄ Hydrolysis. To identify the reaction order with catalyst amount, the H₂ evolution rate is measured by using different catalyst amounts (10, 20, 40, and 80 mg) in the presence of 1 wt% NaBH₄ and 3 wt% NaOH. As shown in Figure 5(a), the addition of even a small amount of Ru/HMS rapidly triggered the hydrolysis of alkaline NaBH₄ with no obvious induction period. And the more the catalyst amount is, the shorter the reaction time required for completing the hydrolysis reaction is. For minimizing the measurement error, the initial stage of NaBH₄ hydrolysis was analyzed to determine the H₂ generation rate, which was then correlated with the catalyst amount to quantitatively estimate its effect on the above-mentioned rate. The H₂ generation rate (mL s⁻¹) was then plotted against
Figure 2: TEM images of Ru/HMS with different magnification times ((a) and (b)), TEM image (c), size distribution (d), and SAED pattern (e) of the deposited Ru nanoparticles and EDS results (f) of Ru/HMS with a Ru loading of 2.3 wt%.

the Ru/HMS catalyst amount (mg), with both terms in the logarithmic scale (Figure 5(b)). A best-fit straight line with the correlation coefficient, $R^2 = 0.989$, is obtained. The slope is $1.12 \approx 1$, demonstrating that the hydrolysis reaction is quasi-first-order with respect to the supplied amount of Ru/HMS. A similar result was also reported by Özkar group in the study of the ammonia borane hydrolysis catalyzed by nanotitania supported Ru nanoparticles [20].

The effect of NaBH$_4$ loading (1, 2.5, 5, and 10 wt%) in the presence of 3 wt% NaOH and 10 mg Ru/HMS catalyst on
the H$_2$ generation rate at 25°C is shown in Figure 6(a). As the NaBH$_4$ concentrations increase from 1 wt% to 10 wt%, the H$_2$ generation rate slightly increased. Generally speaking, an increase in the substrate concentration can generally lead to an increase in the product generation rate. As substrate concentration increases, the solution viscosity also increases. Moreover, the aqueous solubility of NaBO$_2$ (by-product) is low. Accordingly, all these effects in turn lead to the decrease in the H$_2$ generation rate [21]. The effect of NaBH$_4$ loading on the H$_2$ generation rate was also determined by analyzing the initial stage of NaBH$_4$ hydrolysis. From Figure 6(b), a well-fitted straight line with the correlation coefficient, $R^2 = 0.97$, is yielded. The slope is $0.16 \approx 0$, indicating that the hydrolysis of NaBH$_4$ is zero-order with respect to the supplied NaBH$_4$ loading. Yu group and Özkar group also reported similar phenomenon [22, 23].

Based on the above analysis, the rate law of the NaBH$_4$ hydrolysis catalyzed by Ru/HMS can be presented, as shown in

$$-4d[\text{NaBH}_4] = d[\text{H}_2] / dt = k[\text{Ru}],$$

(1)

where $k$ is the rate constant. In view of the effect of NaBH$_4$ loading on the hydrolysis of NaBH$_4$, the zero-order kinetics of NaBH$_4$ loading is limited to below 10 wt% in our study.
3.2.3. Activation Energy of NaBH$_4$ Hydrolysis. Hydrolysis kinetics is thought to be a complex process, which is influenced by many factors, like catalyst performance, temperature, NaBH$_4$ concentration, and so forth. Among them, water is an important reactant for NaBH$_4$ hydrolysis and also solvent for the reactants and by-products [24]. An optimal catalyst amount is expected when the others remain unchanged in NaBH$_4$ hydrolysis reaction. The optimal catalyst amount is evaluated by the value of activation energy ($E_a$). Accordingly, the NaBH$_4$ hydrolysis kinetics is further investigated at different catalyst amount. The effects of temperatures (ranged from 10$^\circ$C to 30$^\circ$C) on the rate of H$_2$ evolved in solutions containing 1 wt% NaBH$_4$ + 3 wt% NaOH and different Ru/HMS amount, that is, 10 mg, 20 mg, 40 mg, and 80 mg, respectively, are shown in Figure 7. As expected, the rate of H$_2$ generation increases with the temperature.

According to Arrhenius equation, the rate constant can be expressed in logarithmic function form, as shown in

$$
\ln k = -\frac{E_a}{RT} + \ln k_0,
$$

where $k$ is the rate constant, $k_0$ is the preexponential parameter, $E_a$ is the activation energy, $R$ is the gas constant (8.314 J · mol$^{-1}$ · K$^{-1}$), and $T$ is the reaction temperature. According to (1), the rate constant $k$ under different catalyst amount can be calculated from the data shown in Figures 7(A)~7(D), respectively. Then the corresponding Arrhenius plots, ln $k$ versus the reciprocal absolute temperature ($1/T$), are shown in Figures 7(a)~7(d), respectively. The slopes of these fitted straight lines were $-11.1$, $-9.8$, $-6.02$, and $-7.69$, corresponding to 10 mg, 20 mg, 40 mg, and 80 mg of Ru/HMS catalyst, respectively. According to the Arrhenius relationship.
Figure 7: Continued.
Figure 7: Volume of H\textsubscript{2} generation against temperature from 1 wt\% NaBH\textsubscript{4} + 3 wt\% NaOH + x g Ru/HMS catalyst and the ln k versus 1/T plots. The error bars reflect around ±5% measurement error of the H\textsubscript{2} generation rate. ((A) and (a)) 0.01 g Ru/HMS; ((B) and (b)) 0.02 g Ru/HMS; ((C) and (c)) 0.04 g Ru/HMS; ((D) and (d)) 0.08 g Ru/HMS.

Figure 8: Activation energy as a function of Ru/HMS amount for the NaBH\textsubscript{4} hydrolysis.

“(2),” the apparent \(E_a\) values for the Ru/HMS-catalyzed hydrolysis of NaBH\textsubscript{4} are calculated as 93.3 ± 1, 81.8 ± 1, 50.1 ± 1, and 63.9 ± 1 kJ/mol, respectively. The dependence of apparent \(E_a\) value on the catalyst amount is also found in our recent work of Ru/MMT-catalyzed NaBH\textsubscript{4} hydrolysis [25].

To observe clearly the changes of apparent \(E_a\) value with catalyst amount, Figure 8 shows the dependence of \(E_a\) value on the catalyst amount when the other catalytic conditions keep the same. It is clearly seen that there exists a valley value between the \(E_a\) value and catalyst amount. Accordingly, the minimum apparent \(E_a\) value can be deduced to be 46.2 ± 1 kJ/mol when the Ru/HMS amount is 52.5 mg. It is commonly believed that the availability of catalytically active sites increases with catalyst amount increasing, and accordingly, lower apparent \(E_a\) value should be obtained. However, increased apparent \(E_a\) value is observed when an excessive catalyst amount is used. The possible reason is that the excess Ru/HMS amount would absorb much water into its pore and hollow region, which resulted in an increased solution viscosity of catalytic system. Accordingly, it becomes difficult for the NaBH\textsubscript{4} molecules to further contact these catalytic active sites and give rise to the mass transport limitations. On the other hand, the low aqueous solubility of by-product, NaBO\textsubscript{2}, would also produce precipitation of NaBO\textsubscript{2}⋅4H\textsubscript{2}O, and two effects might exist: one is to interfere in the mass transfer between Ru/HMS and NaBH\textsubscript{4}; the other is to wrap the surface of Ru/HMS to cover up active sites of catalysts and further prevent NaBH\textsubscript{4} from hydrolysis over active sites [26]. Apparently, there exists an optimal catalyst amount during NaBH\textsubscript{4} hydrolysis. It is important to determine the optimal catalyst amount for optimizing the operating conditions to minimize the use of water in the hydrolysis of NaBH\textsubscript{4}.

Numerous investigations have shown that the studies on the kinetics of the heterogeneous reaction of metal-catalyzed NaBH\textsubscript{4} hydrolysis face two challenges, that is, the controls of temperature and pH during the reaction and the reaction kinetics changes with catalytic conditions, such as catalyst amount, substrate concentration, solution temperature, and reaction time [27]. In our tests, the kinetics of Ru/HMS-catalyzed NaBH\textsubscript{4} hydrolysis is measured under lower temperatures and higher alkalinity to overcome the negative effects by temperature and pH value. Compared to the reported apparent \(E_a\) values obtained in the NaBH\textsubscript{4} hydrolysis as catalyzed by other Ru-based catalysts [14], the apparent \(E_a\) value of the as-prepared Ru/HMS is lower than most of previously reported values except 37.3 kJ/mol for Ru/carbon [28] and 34.9 kJ/mol for Ru/zeolite [29].
3.3. Reusability of Ru/HMS Catalyst. Catalyst reusability is significant in practical application for the H\textsubscript{2} generation. In our study, the reusability of the Ru/HMS was measured by repeating NaBH\textsubscript{4} hydrolysis experiment fifteen times catalyzed by the recycled Ru/HMS batch. After each run, the catalyst was separated from the catalytic mixture by centrifugation and thoroughly washed with copious water to remove the soluble salts. The remaining activity against the cycle time from 1 wt% NaBH\textsubscript{4} + 3 wt% NaOH solution and 40 mg Ru/HMS at 25\textdegree C is shown in Figure 9. As indicated in Figure 9, the remaining activity of Ru/HMS catalyst in the fifth run is only slightly inferior to the initial catalytic activity. The catalyst still preserves 47.7% of its initial catalytic activity and maintains a complete release of H\textsubscript{2} at the 15th runs. The reusability indicates that the Ru/HMS catalyst is separable, redispersible, and yet catalytically active.

To explain the decreased activity of the reused Ru/HMS-catalyzed NaBH\textsubscript{4} hydrolysis in an alkaline solution, XPS is used to detect the chemical changes of the reused Ru/HMS after 15 runs to investigate the reason of the catalytic deterioration of the reused Ru/HMS. As shown in Figure 10, there exists a new peak around 193 eV, which is ascribed to NaBO\textsubscript{2} or B\textsubscript{2}O\textsubscript{3}. The new peak shifts to higher binding energy than elemental B, which is probably due to oxidation. Accordingly, the decreased catalytic activity in subsequent cycles might result from the incorporation of the by-product (NaBO\textsubscript{2}) in the pores of HMS, which would passivate the surface of Ru nanoclusters and decrease the access to active sites. Dai et al. in their study of the Ru/MMT-catalyzed hydrolysis of ammonia borane also reported similar result [30]. Additionally, the decreased activity also might result from the catalyst material loss during the separation and redispersion [31].

4. Conclusions

In summary, a facile method for preparing the Ru/HMS composites as highly active nanocatalyst is developed for hydrolyzing sodium borohydride from its alkaline solution. Different Ru loadings in Ru/HMS are successfully achieved, and the Ru/HMS with a Ru loading of 2.3 wt% shows the highest catalytic activity. When the Ru/HMS catalyst with a Ru loading of 2.3 wt% is used, a maximum H\textsubscript{2} generation rate of 18.6 L min\textsuperscript{−1} g\textsuperscript{−1} (Ru) from 1 wt% NaBH\textsubscript{4} + 3 wt% NaOH solutions at 25\textdegree C is obtained. The relation of activation energy versus catalyst amount is constructed to optimize the catalyst amount; and the minimum apparent $E_a$ value obtained from the fitted curve is 46.2 $±$ 1 kJ/mol when the catalyst amount was 52.5 mg, lower than the $E_a$ values of most Ru-based heterogeneous catalysts reported in literatures. Moreover, the reusability of the catalyst shows that the remaining activity of Ru/HMS catalyst in the fifth run is only slightly inferior to that in the first run, when, at the fifteen times of usage, the catalyst still preserves 47.7% of its initial catalytic activity. The decreased catalytic activity in subsequent cycles might result from the incorporation of the by-product (NaBO\textsubscript{2}) in the pores of HMS, which would passivate the surface of Ru nanoclusters and decrease the access to active sites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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