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Oxygen-vacancy-rich Ru-clusters decorated Co/Ce oxides modifying ZIF-67 nanocubes as a high-efficient catalyst for NaBH₄ hydrolysis

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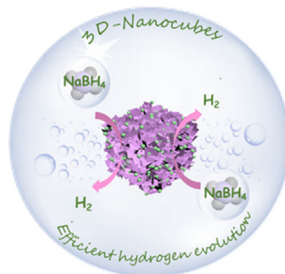
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HIGHLIGHTS

- Ru/Co₆Ce₁@ZIF-67 nanocubes are fabricated by surfactant-mediated and reduction methods.
- The catalyst shows a high HGR and TOF (413.9 min⁻¹) surpassing most recently reported catalysts.
- The catalyst exhibits a stable multi-cycle reusability for NaBH₄ hydrolysis.
- Oxygen vacancies and the synergy between different components are the keys to improve catalytic activity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 July 2022
Received in revised form
26 August 2022
Accepted 29 August 2022
Available online xxx

Keywords:

Ru/Co₆Ce₁@ZIF-67 catalyst
Oxygen vacancies

ABSTRACT

Designing a cost-effective and high-performance catalyst for NaBH₄ hydrolysis is a significant step in developing a sustainable hydrogen source. Herein, we prepared a cost-effective Ru-clusters decorated cobalt-cerium oxides coating ZIF-67 (Ru/Co₆Ce₁@ZIF-67) catalyst via a facile reduction method, displaying high performance and exceptional reusability in alkaline NaBH₄ solution. The optimized catalyst exhibits a high hydrogen generation rate (HGR, 5726.1 mL min⁻¹ g⁻¹), turnover frequency (TOF, 413.9 mol_{H₂} min⁻¹ mol_{Ru}⁻¹), and low activation energy (E_a, 53.0 kJ mol⁻¹), surpassing most of the recently reported catalysts. Furthermore, the catalytic performance does not change considerably after five cycles, indicating the catalyst's multi-cycle reusability. Studies imply the uniquely

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<https://doi.org/10.1016/j.ijhydene.2022.08.289>

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NaBH₄ hydrolysis
Hydrogen generation

synergistic effect of Ru, Co/Ce oxides, abundant oxygen vacancies, as well as the porous nanocube structure, enabling the catalysts to possess high metal dispersion, outstanding catalytic performance and exceptional reusability. This work will open light on using an oxygen vacancies-rich strategy to design a high-activity catalyst for promoting NaBH₄ hydrolysis.

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Introduction

Energy shortage and environmental pollution are the main factors affecting the quality of life [1]. There is a desperate need to mine green, renewable and efficient energy materials [2,3]. Hydrogen is an ideal alternative to traditional fuels due to its high energy density and zero CO₂ emission [4,5]. However, finding a cheap hydrogen storage method is often very challenging. NaBH₄ is a promising candidate among the various storage materials because of its high theoretical hydrogen content of 10.6 wt%, long-term stability in alkaline condition and nontoxicity [6,7]. NaBH₄ can also generate H₂ through hydrolysis under mild conditions, and the by-products are non-toxic [8]. Moreover, a recent study indicated that the NaBH₄ could be regenerated through by-product rehydrogenation, making it possible for the NaBH₄-H₂-PEMFC system to be a primary source for on-demand power supply [9]. Nevertheless, the self-hydrolysis of NaBH₄ releases H₂ slowly, and the overall conversion is only 7–8% at ambient temperature [10,11]. Consequently, designing efficient catalysts to promote sodium borohydride hydrolysis remains a critical issue.

Previous studies suggested that noble metal-based catalysts, such as Ru-Co-PEDOT [12] and Ru-Fe/Go [13], showed excellent catalytic activity and robust stability toward NaBH₄ hydrolysis [14]. However, the high cost, the lack of reserves, and the self-agglomeration limit industrial application [15,16]. Therefore, considerable effort has been dedicated to developing non-noble transition metals. Recently, cobalt-based catalysts are widely studied for hydrolysis of sodium borohydride due to the fact that its performance is particularly validated as the most effective non-noble metal among Ni-, Fe-, and Cu-based catalysts [17]. Among cobalt-based catalysts, cobalt oxides have been confirmed to be efficient catalyst [18]. Wei et al. [19] reported that Co₃O₄ hollow fiber catalyst exhibited good performance. However, the activity and stability of cobalt oxides catalysts were still lower than those of noble metal catalysts [20]. Many noble metal and cobalt oxide composite catalysts have been developed to achieve high performance while reducing costs. For example, Dou et al. [21] reported a high-efficiency Ru-clusters decorated CoO_x@NPC catalyst for hydrogen generation.

To address the aggregation of the metal nanoparticles during synthesis, suitable supports or organic capping agents should be introduced. Metal-organic frameworks (MOFs) are considered ideal support materials due to their unique properties, including exceptional porosity, structural diversity, large specific surface area, and chemical stability [22,23]. ZIF-67 is one of MOFs with imidazole as an organic linker with metal cobalt, which has a large specific surface area to prevent

metal particles agglomeration and has proven to be highly stable in solution, even in alkaline solution at high temperatures [24,25]. Many studies have also shown that ZIF-67-supported composites catalysts exhibit remarkable performance in NaBH₄ hydrolysis for hydrogen production, e.g., Pd/PD-ZIF-67 [15], Ru/ZIF-67 [26] and so on. Given these merits, ZIF-67 appears to be an excellent substrate to promote NaBH₄ hydrolysis. Nonetheless, MOFs as carriers have low electrical conductivity, hindering the charge transfer during hydrolysis [27]. It can enhance electron transport by introducing oxygen vacancies created by rare earth elements, such as cerium oxide [28]. In cerium oxides, Ce³⁺ and Ce⁴⁺ coexist, and the electronic structure of Co species can be modified due to the existence of electronically flexible transitions and abundant oxygen vacancies between Ce³⁺ and Ce⁴⁺, thereby enhancing the conductivity of Co-MOF and improving the performance of the catalyst [29,30]. Based on the above consideration, we assume that Ru cluster-modified Co oxides and doped Ce oxides have the potential to be an efficient catalyst for hydrolysis of sodium borohydride.

Here, we propose a facile surfactant-mediated and chemical reduction method to synthesize Ru/Co₆Ce₁@ZIF-67 catalyst with abundant oxygen vacancies for NaBH₄ hydrolysis in alkaline environments. The Ru clusters (~2.7 nm) decorated Co₆Ce₁@ZIF-67 nanocubes showed outstanding catalytic activity and remarkable reusability for NaBH₄ hydrolysis. It has a high HGR value of 5726.1 mL min⁻¹ g⁻¹ and a TOF value of 413.9 mol_{H₂} min⁻¹ mol_{Ru}⁻¹. Systematic investigations further demonstrate that the ZIF-67 support prevents Ru clusters aggregation, and oxygen vacancies can accelerate electronic transfer, promoting the reversible dissociation of B-H on active sites of Co oxides and Ru clusters, and finally stimulating hydrolysis of sodium borohydride. Furthermore, we proposed a plausible reaction mechanism according to the Michaelis-Menten model reported in the previous literature [31].

Experimental section

Materials

Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99.0%, Aladdin), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.95%, Macklin), ruthenium (III) trichloride (RuCl₃·xH₂O, 99%, Ru:37–40%, Innochem), 2-methylimidazole (2-MI, 98%, Aladdin), cetyltrimethylammonium bromide (CTAB, 99.0%, Aladdin), sodium borohydride (NaBH₄ ≥ 98.0%, Sinopharm Group), sodium hydroxide (NaOH ≥ 96.0%, Xilong Science), ethanol (99.7%, Kelongchem). All chemicals were purchased from commercial

companies and could be used directly without further purification.

Synthesis of ZIF-67 nanocubes

Co-based zeolitic imidazolate framework (ZIF-67) nanocubes were prepared according to previous work with slightly modification [32]. In a typical procedure, 580 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL of deionized water containing 10 mg of CTAB. Then, this solution was rapidly injected into 140 mL of an aqueous solution containing 908 mg of 2-methylimidazole and stirred at room temperature for 20 min. The purple product was collected by centrifugation, washed three times with ethanol and vacuum-dried at 70 °C for 12 h.

Synthesis of $\text{Co}_6\text{Ce}_1@ZIF-67$

A total of 60 mg of ZIF-67 nanocubes was dispersed in 40 mL of ethanol to form solution A. 160 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 40 mg of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 10 mL of ethanol to form solution B. Then, solution B was dripped on solution A under magnetic stirring and sonicated for 40 min to form a uniform solution. Finally, the product was collected by centrifugation, washed with ethanol three times, and vacuum-dried at 70 °C for 12 h. For comparison, under keeping the total mass of the metal salt at 0.2 g, other $\text{CoCe}@ZIF-67$ composites were prepared by altering the Co/Ce molar ratio (1:1, 4:1, 6:1, 9:1, 12:1) during the synthesis process. The $\text{Co}@ZIF-67$ and $\text{Ce}@ZIF-67$ were prepared via the same routine without adding $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Synthesis of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$

The $\text{Co}_6\text{Ce}_1@ZIF-67$ (80 mg) was added into a 50 mL glass beaker with 20 mL of deionized water and 15 mg of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$. After continuous stirring for 4 h, 10 mL of 2.6 M NaBH_4 solution (including 2 wt% NaOH) was added dropwise into the above mixture. After stirring for another 0.5 h, the resultant product crystal was separated by centrifugation, followed by multiple times washing in deionized water and ethanol, and subsequently dried in a vacuum at 70 °C for 12 h. Inductive coupled plasma atomic emission spectroscopy (ICP-AES) accurately determined the content of Ru species (Table S1) and the sample with 6.3 wt% showed the highest catalytic performance. Samples with Ru loadings of 4.5 wt% to 10.6 wt% were prepared by the same method, using $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with different mass. As a comparison, a mass ratio of 6.3 wt% Ru was applied to synthesize all other contrastive catalysts. The $\text{Ru}/\text{Co}@ZIF-67$ and $\text{Ru}/\text{Ce}@ZIF-67$ were prepared using the same procedure mentioned above without $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In addition, $\text{Ru}@ZIF-67$ was synthesized by directly adding $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ into ZIF-67 solution, followed by a similar reduction treatment.

Synthesis of single Ru

200 mg of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was dissolved in 40 mL of deionized water via ultrasonication. After continuous stirring for 30 min, 10 mL of NaBH_4 solution was added into the above mixture.

Finally, the black mixture was centrifuged to collect the sediment, which was washed at least three times with deionized water and ethanol, then dried under vacuum.

Catalytic hydrolysis of NaBH_4 measurements

The evolved hydrogen from the hydrolysis of NaBH_4 was collected and measured with a drainage method. A mixed solution of 25 mL, containing 150 mL NaBH_4 and 0.4 wt% NaOH, was injected to a three-necked round-bottom flask (100 mL), placed into a temperature-controlled water bath oscillator to keep it at 25 °C during the hydrolysis reaction. After 0.5 h, the prepared catalysts (10 mg) were dispersed in the above solution, rapidly plugging the flask. The instantaneous water volume changes were monitored by an electronic balance connected to a computer. Hydrolysis of NaBH_4 was also carried out at different temperatures (298–318 K) to obtain the activation energy. For the reusability study, the catalyst was recollected, washed with deionized water and ethanol, and dried in a vacuum at 70 °C after each cycle. The collected catalyst from the previous test was transferred to each process's new test solution. It was worth noting that the amount of motivation was the same as in the first cycle experiment. All tests were repeated three times to ensure reliable results.

Results and discussion

Synthetic method and crystallinity analysis

The design strategy of the $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$ is illustrated in Fig. 1a. Firstly, ZIF-67 nanocubes are prepared through a surfactant-mediated method. Afterward, the as-prepared ZIF-67 nanocubes were mixed with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to form Co–Ce oxides on the surface of ZIF-67 nanocubes. Finally, the Ru species are introduced into the $\text{Co}_6\text{Ce}_1@ZIF-67$ by an ambient temperature reduction for producing the $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$. The crystallinity of as-prepared catalysts is first analyzed by X-ray diffraction (XRD). As shown in Fig. 1b, pure ZIF-67 nanocubes and $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$ share the same XRD patterns, while the intensity of the peaks varies between them. However, there is no apparent diffraction peak of the cobalt-cerium oxides, implying the low-loading and/or amorphous nature of the composite. Such amorphous characteristics are beneficial for catalytic materials with higher performance than crystalline material because they can supply larger ion-accessible surface area and sufficient redox-active centers [33]. Furthermore, no characteristic peaks of Ru clusters are observed in the XRD pattern of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$ due to the low Ru loading, which the fuzzy lattice fringes can confirm in the TEM images of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$ [34]. As shown in Fig. 1c, we resort to the electron paramagnetic resonance (EPR) spectra for direct oxygen vacancies identification. The apparent symmetrical signals at $g = 2.003$ correspond to oxygen vacancies of the samples [35]. An increase in the oxygen vacancy signal intensity is observed after introducing the Ce component in $\text{Ru}/\text{Co}@ZIF-67$, which can massively alter the electronic properties of the composite, thereby enhancing the catalytic activity [36].

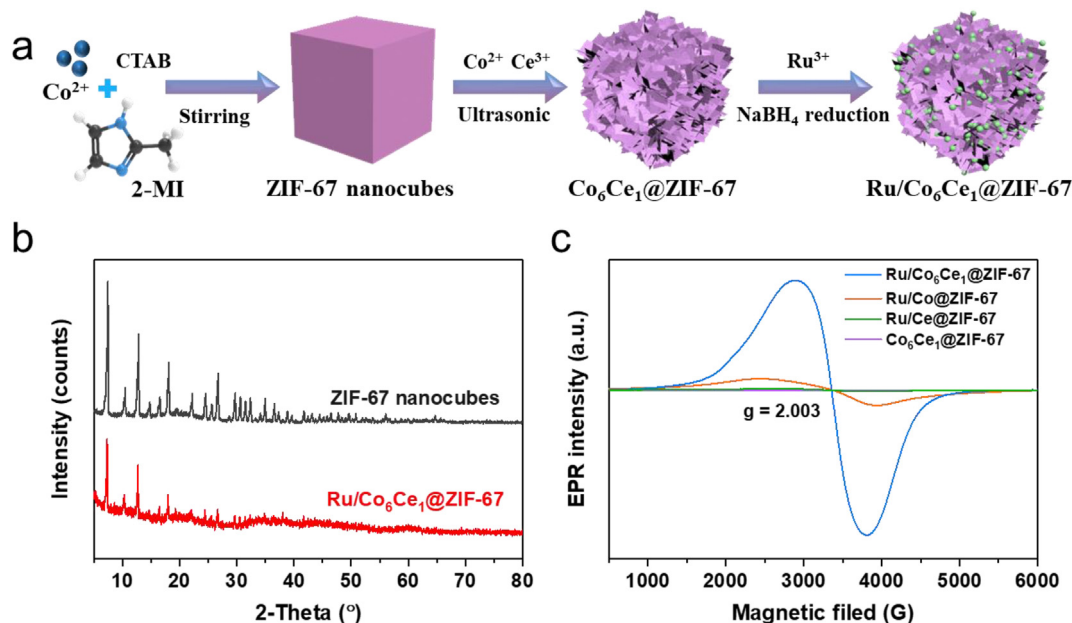


Fig. 1 – (a) Schematic diagram of the synthesis of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$. (b) XRD patterns of ZIF-67 nanocubes and $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$. (c) EPR spectra of the synthesized $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$, $\text{Ru}/\text{Co}@ZIF-67$, $\text{Ru}/\text{Ce}@ZIF-67$ and $\text{Co}_6\text{Ce}_1@ZIF-67$.

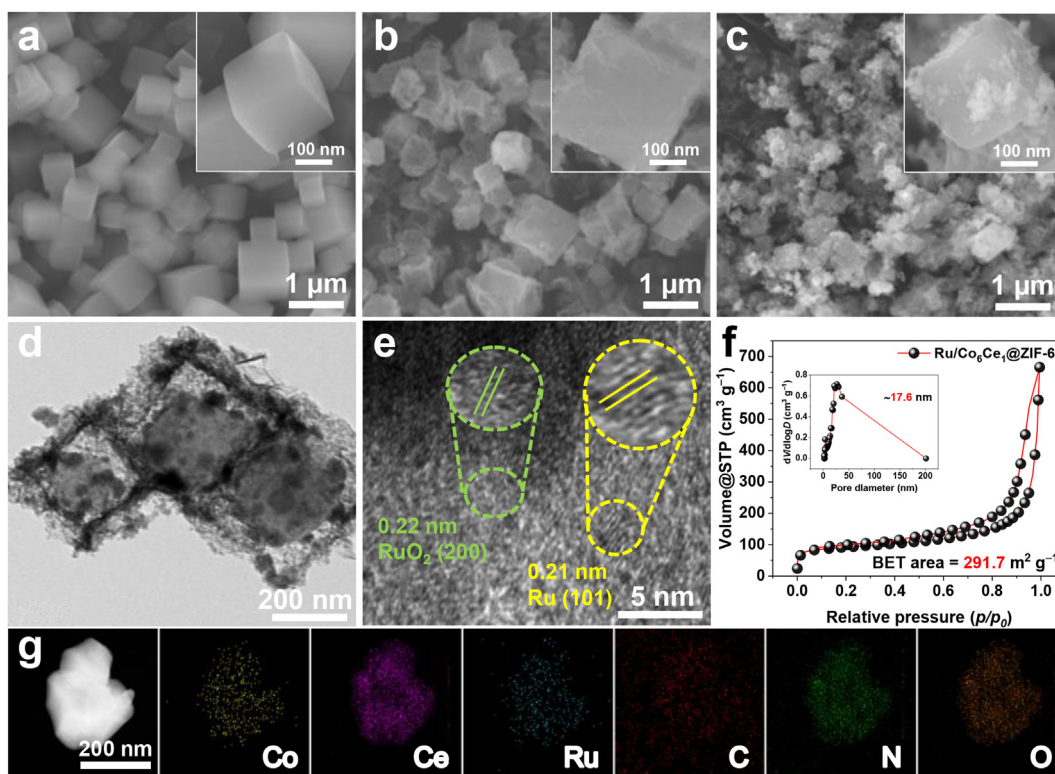


Fig. 2 – Scanning electron microscopy (SEM) of (a) ZIF-67 nanocubes, (b) $\text{Co}_6\text{Ce}_1@ZIF-67$ and (c) $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$ (Insets are high-magnification SEM images). (d) Transmission electron microscopy (TEM) and (e) high-resolution TEM images of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$. (f) N_2 adsorption/desorption isotherms with pore-size distribution curve (inset) of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$. (g) HAADF-STEM image of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$ and corresponding elemental mappings of Co, Ce, Ru, C, N, and O.

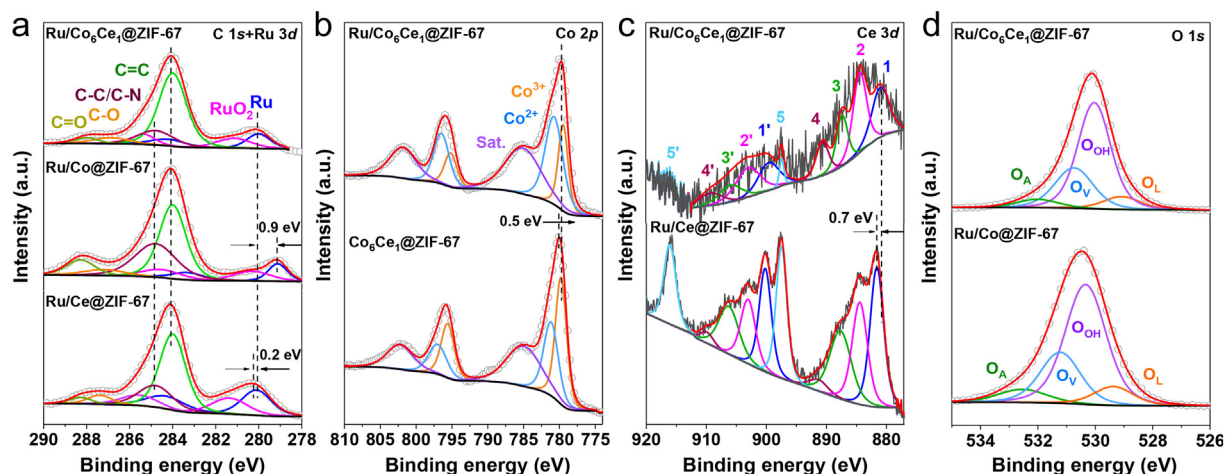


Fig. 3 – High-resolution XPS spectra of (a) C 1s + Ru 3d, (b) Co 2p, (c) Ce 3d and (d) O 1s regions of Ru/Co₆Ce₁@ZIF-67, Ru/Co@ZIF-67, Ru/Ce@ZIF-67 and Co₆Ce₁@ZIF-67, respectively.

Microstructure analysis

The morphological features and microstructure of the catalysts are analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2a shows the as-formed ZIF-67 nanocube morphology with a smooth surface. The further reaction with excess Co(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O under sonication for 40 min leads to formation of Co₆Ce₁@ZIF-67 nanocubes. Fig. 2b reveals that the SEM image of Co₆Ce₁@ZIF-67 nanocubes still maintains the cubic shape. But the surface of the products become rough, and the higher magnification image displays that the Co₆Ce₁ oxides appear to be a nanosheet. After introducing Ru, the sample has cubic characteristics with some distended nanoparticles on the surface, loosely stacked together (Fig. 2c). These results suggest that introducing a specific number of Co/Ce oxides and Ru clusters does not destroy the cube-like framework of the ZIF-67-based derivative. As shown in Fig. 2d, the TEM image shows that Ru/Co₆Ce₁@ZIF-67 exhibits a yolk-shell structure consisting of solid ZIF-67 yolk and Ru/Co₆Ce₁ shell, similar to the literature reports [37,38]. Each nanocube is uniformly decorated with dark Ru clusters with a size of ~2.7 nm (Fig. S1). According to the high-resolution TEM image of Ru/Co₆Ce₁@ZIF-67, Fig. 2e shows that the lattice spacing of 0.21 nm are indexed to Ru (101) crystal plane [39]. The interplanar spacing of 0.22 nm are attributed to the (200) crystal plane of RuO₂ [40]. The N₂ adsorption–desorption isotherms of Ru/Co₆Ce₁@ZIF-67 displays the type IV isotherm with a remarkable hysteresis loop, indicating the existence of mesopores [41]. The Brunauer-Emmett-Teller (BET) specific surface area and pore size are 291.7 m² g⁻¹ and ~17.6 nm (Fig. 2f). These results show that the multiporous 3D frame structure and high surface area of Ru/Co₆Ce₁@ZIF-67 benefit ions' fast diffusion and expose more active sites, which can enhance the catalytic activity [42,43]. In addition, the EDX spectrum (Fig. S2) manifests the presence of Ru, Co, Ce, C, N, and O, and elemental mapping images elucidate that all the elements are homogeneously distributed throughout the Ru/Co₆Ce₁@ZIF-67 catalyst (Fig. 2g).

X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) has been further conducted to investigate the relationship between the charge and chemical valence states on the surface of the catalysts. As shown in Fig. S3, the XPS survey spectra of Ru/Co₆Ce₁@ZIF-67 verify the presence of C, N, O, Co, Ce and Ru elements, agreeing well with the above HAADF-STEM elemental mapping and EDX results. The high-resolution C 1s + Ru 3d spectrum (Fig. 3a) are deconvoluted into C=C (284.0 eV), C–C (284.8 eV) and used as a calibration standard [44]. The two peaks at 280.0 and 284.2 eV binding energies attribute to metallic Ru⁰ [21], whereas the peaks at 281.2 eV and 285.4 eV correspond to RuO₂. This surface oxide could be formed from exposure of the samples to atmosphere during the reaction. Compared to the Ru/Co@ZIF-67, the binding energy of Ru is positively shifted by 0.9 eV, indicating that the Ce doping can effectively tune the electronic structure of Ru/Co₆Ce₁@ZIF-67, thereby regulating efficient charge transfer [45]. Compared with the Ru/Ce@ZIF-67 sample, the binding energy of Ru is negatively shifted by 0.2 eV, which indicates that there is a strong charge-transfer interaction between Ru clusters and Co oxides [46]. Fig. 3b displays the Co 2p high-resolution spectrum, where the binding energies of 779.5, 780.8 and 785.3 eV can be coincided with Co³⁺, Co²⁺, and the satellite peak [47]. The binding energies of Co on Ru/Co₆Ce₁@ZIF-67 exhibit a negative shift compared to the Co₆Ce₁@ZIF-67, which confirms that the introduction of Ru clusters has a great influence on the electronic states of the surrounding Co atoms. Typically, the Co²⁺/Co³⁺ ratio of the Ru/Co₆Ce₁@ZIF-67 is higher than that of Co₆Ce₁@ZIF-67, suggesting that the part of Co³⁺ is reduced to Co²⁺ after introducing Ru to create oxygen vacancies [48]. Interestingly, it has been reported that oxygen vacancies can accelerate electronic transfer and increase the conductivity of the catalyst, laying the foundation for improving catalytic performance [49,50].

The Ce 3d spectrum of Ru/Co₆Ce₁@ZIF-67 is fitted with five pairs of spin-energy separations (Fig. 3c). The characteristic peaks located at 880.9 eV, 887.3 eV (1, 3) and 899.5 eV, 905.9 eV

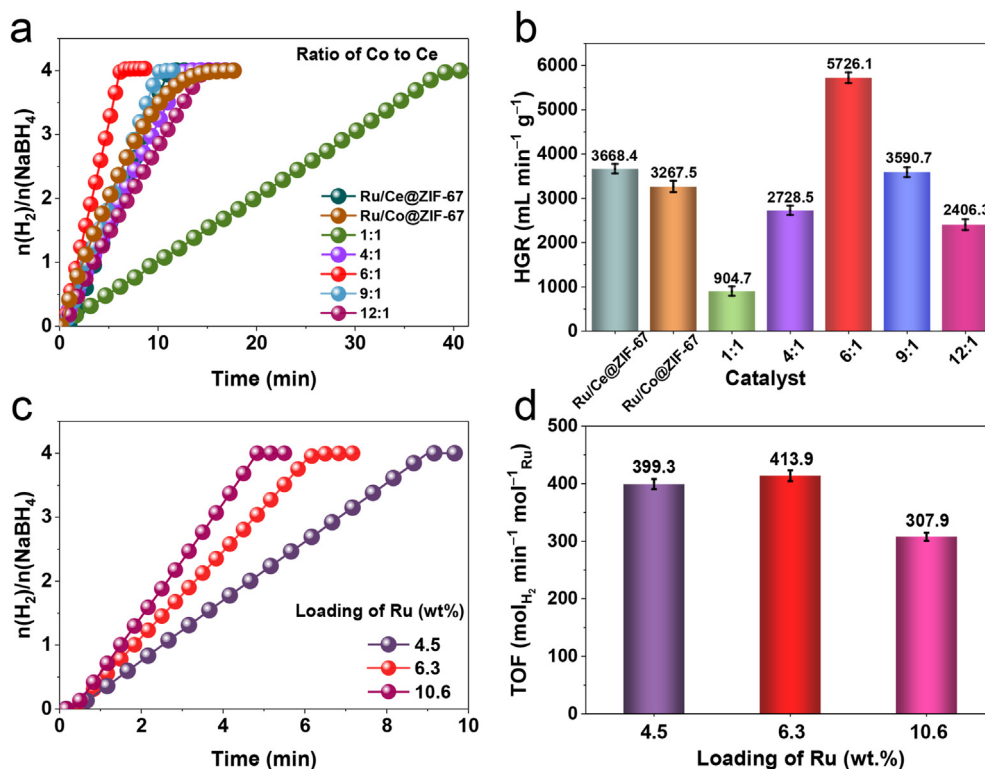


Fig. 4 – (a) Curves of hydrolysis of alkaline NaBH₄ solution with different ratios of Co/Ce, and (b) the corresponding H₂ evolution rate values. (c) Curves of hydrolysis of alkaline NaBH₄ solution with different loadings of Ru species on Ru/Co₆Ce₁@ZIF-67 catalysts, and (d) the summarized TOF values.

(1', 3') are assigned to Ce³⁺ (3d¹⁰4f¹ initial electronic state), whereas the six peaks at 884.4 eV, 890.6 eV, 897.4 eV (2, 4, 5) and 903.0 eV, 909.2 eV, 916.0 eV (2', 4', 5') are attributed to Ce⁴⁺ (3d¹⁰4f⁰ initial electronic state) [51,52]. In the Ce 3d spectra, the Ce³⁺ co-exists with Ce⁴⁺ in the composite [53]. Clearly, the peak of Ce³⁺ in Ru/Co₆Ce₁@ZIF-67 shows a negative shift of about 0.7 eV compared to Ru/Ce@ZIF-67, implying the electrostatic interactions between Ce oxides and surrounding Co oxides. It is worth noting that the Ce³⁺ ions interact with surrounding atoms such as Co through lone electron existing in the 4f¹ orbital. In addition, oxygen vacancies can be created on the catalyst surface due to the charge compensation of Ce³⁺ ions [54]. The above analyses prove that the introduction of Ce can generate more oxygen vacancies, thereby enhancing the catalyst's performance [55]. Furthermore, we detect the oxygen vacancies by O 1s XPS spectra. Fig. 3d shows that the O 1s spectra can be deconvoluted into four peaks. The peaks of ~529.1 eV, ~530.0 eV, ~530.7 eV and ~532.0 eV can be attributed to lattice oxygen (O_L), oxygen atoms bound to hydroxyl species (O_{OH}), oxygen vacancy (O_v) and absorbed oxygen (O_A), respectively [56,57]. The integral area ratio of oxygen vacancy peaks in Ru/Co₆Ce₁@ZIF-67 (26.3%) is more significant than that in Ru/Co@ZIF-67 (24.6%), implying that oxygen vacancies increase after the introduction of Ce component, which is in line with the EPR results.

Catalytic hydrolysis analysis

The catalytic activities are assessed in alkaline NaBH₄ solution at 25 °C, and the volume of H₂ is measured by a water

displacement method. The hydrolysis setup is schematically illustrated in Fig. S4. The NaBH₄ (150 mM) aqueous solution shows almost no self-hydrolysis (Fig. S5), and negligible hydrogen gas is produced from 150 mM NaBH₄ + 0.4 wt% NaOH solution indicating NaBH₄ is stable in both water and under an alkaline solution (Fig. S6). As shown in Fig. 4a and b, we investigate the effect of catalysts fabricated by different molar ratios of Co/Ce on H₂ generation. When the molar ratio of Co/Ce is 6:1, Ru/Co₆Ce₁@ZIF-67 exhibits the best activity and is superior to those of Ru/Co@ZIF-67 and Ru/Ce@ZIF-67. And the HGR value is superior to those currently reported literature (Table S2). Simultaneously, the optimal Ru loading has been researched in great detail. As displayed in Fig. 4c–d, a higher Ru loading shows a higher H₂ release rate, but the TOF values show a volcano-shape curve. When the content of Ru is 6.3 wt %, the corresponding TOF reaches a maximum value of 413.9 mol_{H₂} min⁻¹ mol⁻¹_{Ru}.

As shown in Fig. 5a and b, the Ru/Co₆Ce₁@ZIF-67 catalyst only takes about 6 min to achieve the complete hydrolysis of sodium borohydride. Notably, for Ru/ZIF-67 and Ru catalysts, sodium borohydride hydrolyzed only about 35% and 10% within 6 min, while Co₆Ce₁@ZIF-67 and ZIF-67 had almost no activity. These results showed that Ru/Co₆Ce₁@ZIF-67 exhibited the highest performance relative to all control catalysts, indicating that Ru is the predominate active site and Co₆Ce₁@ZIF-67 plays a crucial role in catalytic hydrolysis [58]. The analysis suggests that the synergistic effect of different components and abundant oxygen vacancies in the Ru/Co₆Ce₁@ZIF-67 hybrid catalyst are the main factors for the high catalytic performance. The influence of NaBH₄ concentration

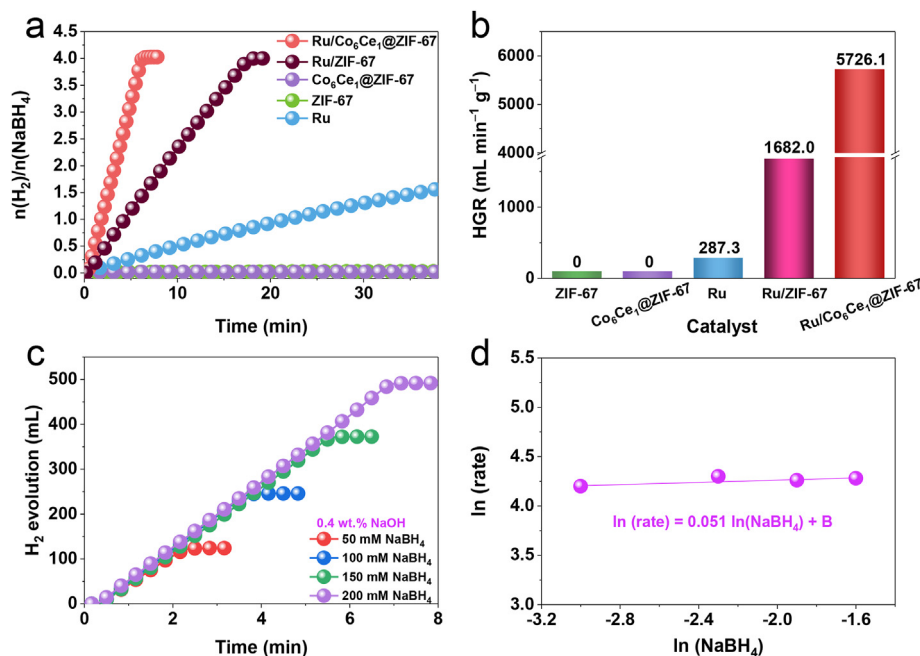


Fig. 5 – (a) Curves of hydrolysis of alkaline NaBH_4 solution with different kinds of catalysts, and (b) the corresponding H_2 evolution rate values. (c) The relationship between H_2 evolution and different NaBH_4 concentrations and (d) the corresponding plot of $\ln(\text{rate})$ vs $\ln(\text{concentration of } \text{NaBH}_4)$.

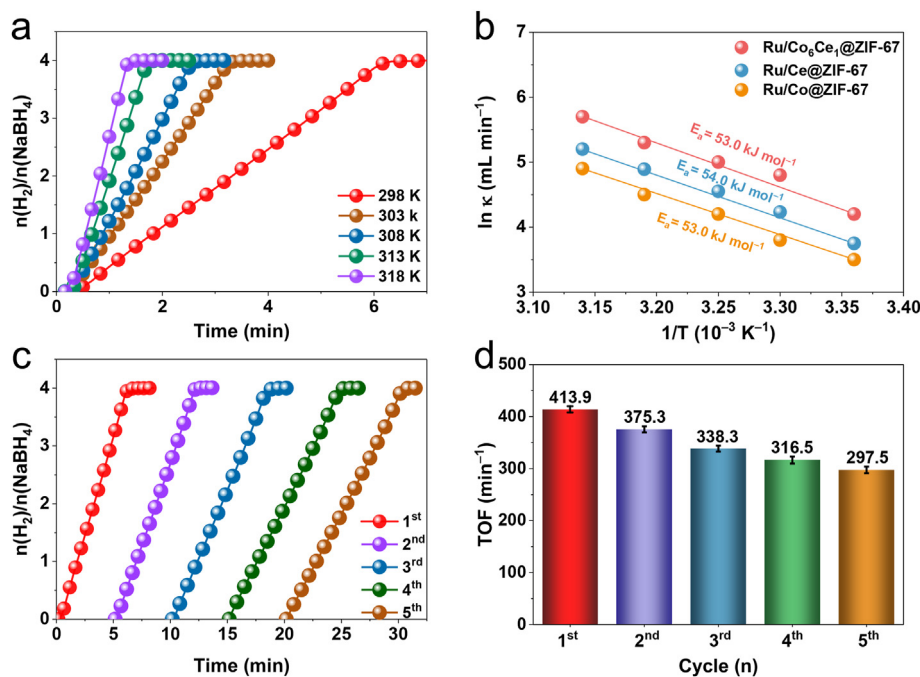


Fig. 6 – (a) Curves of hydrolysis of alkaline NaBH_4 solution with different reaction temperatures, and (b) the calculated activation energies of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$, $\text{Ru}/\text{Co}@ZIF-67$ and $\text{Ru}/\text{Ce}@ZIF-67$ catalysts. (c) Recycling stability test of $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$ catalyst in alkaline NaBH_4 solution at 25°C and (d) the corresponding TOF values in the different recycling test.

has also been explored at 25°C with 10 mg $\text{Ru}/\text{Co}_6\text{Ce}_1@ZIF-67$. Fig. 5c reveals that the hydrogen generation rate does not change significantly. Meanwhile, the relation between $\ln(\text{rate})$ and $\ln(\text{NaBH}_4)$ has been given in Fig. 5d, where the slope value

is calculated to be 0.051, which is negligible and indicates a zero-order reaction kinetics [59]. NaOH is often used as a stabilizing agent to prevent the self-hydrolysis of NaBH_4 . Fig. S7 shows the effect of NaOH concentration on hydrogen

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2022.08.289>.

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