Highly dispersed Ru/Co catalyst with enhanced activity for catalyzing NaBH<sub>4</sub> hydrolysis in alkaline solution

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#### Communication

# Highly dispersed Ru/Co catalyst with enhanced activity for catalyzing NaBH<sub>4</sub> hydrolysis in alkaline solution

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E-mail address: <u>donghua@iccas.ac.cn</u> (H. Dong). Graphical abstract



A  $TiO_2$  supported Ru/Co complex catalyst which was highly active for catalyzing NaBH<sub>4</sub> hydrolysis in alkaline solution was fabricated. The Ru efficiency of the fabricated catalyst was higher than most of the recently reported Rubased catalysts.

ARTICLE INFO	ABSTRACT
Article history: Received 5 March 2020 Received in revised form 16 March 2020 Accepted 23 March 2020 Available online	Ru and Co are highly dispersed on the surface of TiO <sub>2</sub> nanoparticles with an easy coprecipitation method to fabricate a novel Ru-based catalyst (Ru/Co-TiO <sub>2</sub> ). The fabricated Ru/Co-TiO <sub>2</sub> catalyst exhibits superior catalytic performance for promoting NaBH <sub>4</sub> hydrolysis in alkaline medium, showing an impressive hydrogen generation rate per gram Ru as high as 172 L min <sup>-1</sup> g <sub>Ru</sub> <sup>-1</sup> , which is better than most of recently reported Ru-based catalysts. In addition, the fabricated Ru/Co-TiO <sub>2</sub> catalyst also shows excellent durability in cycle use, with only 2.9% activity loss after being used for 5 cycles. These advantages make the developed Ru/Co-TiO <sub>2</sub> catalyst a potential choice for promoting hydrogen generation from NaBH <sub>4</sub> hydrolysis.
Keywords: Ru/Co NaBH <sub>4</sub> Catalytic hydrolysis Hydrogen generation Heterogeneous catalysis	

Due to the distinct advantages including stability, high hydrogen storage capacity, hydrolysis controllability and high hydrogen purity, borohydrides form a kind of very promising hydrogen storage materials [1-5]. A typical representative of them is sodium borohydride (NaBH<sub>4</sub>) [6,7]. The hydrolysis of 1 g NaBH<sub>4</sub> can release 0.21 g hydrogen with high purity. However, the self-hydrolysis of NaBH<sub>4</sub> without a catalyst is extremely slow [7,8]. Therefore, great efforts have been made to develop suitable catalysts which could endow NaBH<sub>4</sub> hydrolysis decent rates [9-11].

Varieties of metal catalysts, such as Ru [12-19], Pd [13,20], Co [21-32], Ni [32-36] and complexes of them [37-46], were extensively studied in the last years. Plenty of researches suggest that Ru-based catalysts have excellent activity in catalyzing NaBH<sub>4</sub> hydrolysis [8,12-15,40,41]. Nevertheless, although monometallic Ru catalysts have high activity for catalyzing NaBH<sub>4</sub> hydrolysis under neutral conditions, their performance is dramatically compromised under alkaline conditions [19,38]. Yet, NaBH<sub>4</sub> solution is usually stabilized in alkaline environment to prevent the uncontrolled self-hydrolysis. On the contrary, when Ru is combined with other metals, the formed complex catalysts could maintain the high catalytic activity for NaBH<sub>4</sub> hydrolysis under alkaline conditions [15,41]. Furthermore, considering the high cost and scarcity of Ru metal, it is very important to develop catalysts with special composition and nano/microstructures to improve the Ru efficiency. For this propose, Ru species in the catalysts must be dispersed well enough. It means

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that the catalysts composed of Ru nanoparticles, clusters, or even single atoms are highly demanded. However, free Ru nanoparticles, clusters, or single atoms are not stable. They tend to aggregate to reduce the surface energy. Thus, varieties of substrates have been employed to support Ru species to improve their stability [12-15,40-43]. Nevertheless, Ru species in these catalysts is normally in the form of nanoparticles, leaving space for further reducing the size to improve the catalytic efficiency.

Herein, we report a novel Ru-based catalyst (Ru/Co-TiO<sub>2</sub>), which was fabricated through coprecipitation of  $Ru^{3+}$  and  $Co^{2+}$  on TiO<sub>2</sub> nanoparticles in aqua regia. Ru and Co species in this catalyst were well dispersed. NaBH<sub>4</sub> hydrolysis experiments in alkaline solutions showed that the Ru/Co-TiO<sub>2</sub> catalyst had superior catalytic activity and durability.



Scheme 1. Schematic illustration of the fabrication of Ru/Co-TiO<sub>2</sub>.

Scheme 1 shows an illustration of the fabrication of the Ru/Co-TiO<sub>2</sub> catalyst. Briefly, RuCl<sub>3</sub>•3H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O were firstly dissolved in aqua regia to form a homogenous solution, into which TiO<sub>2</sub> nanoparticles (~40 nm) were added. The mixture was stirred in 140 °C oil bath until it was dry. The obtained solid was then reduced in aqueous solution of ammonia borane, washed with water and dried at 60 °C in vacuum overnight to obtain Ru/Co-TiO<sub>2</sub> catalyst. Ru-TiO<sub>2</sub> and Co-TiO<sub>2</sub> were fabricated for control experiments with the same method, but without Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O or RuCl<sub>3</sub>•3H<sub>2</sub>O in the original aqua regia solutions, respectively.

After the successful fabrication, the loading density of Ru and Co in the catalysts was measured with ICP-OES. The results demonstrated that  $Ru/Co-TiO_2$  catalyst had 0.06 wt% Ru and 0.61 wt% Co, while  $Ru-TiO_2$  and  $Co-TiO_2$  had 0.09 wt% Ru and 0.77 wt% Co, respectively. The Brunauer-Emmett-Teller (BET) surface measurement indicated that  $TiO_2$  nanoparticles used as the substrate had a specific surface area of 64.3 m<sup>2</sup>/g. Considering the low density of Ru and Co, the high surface area of  $TiO_2$  could provide sufficient space for them to anchor.

Transmission electron microscopy (TEM) and high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images in Fig. 1 have shown the structures of the fabricated Ru/Co-TiO<sub>2</sub> catalyst. The lattice fringes highlighted in Fig. 1b show the planes with interplanar spacing of 3.5 Å, corresponding to the (101) planes of TiO<sub>2</sub>. However, due to their far lower density than Ti, no distinct Co and Ru atoms could be observed with HAADF-STEM, which is consistent with the results previously reported by Tao *et al.* [47]. This also verified the good distribution of Co and Ru species in the sample. As Co and Ru species could not be observed directly from HAADF-STEM images, elemental mapping was carried out to verify their existence (Fig. 1c). It could be clearly seen that the Co and Ru species sparsely dispersed on TiO<sub>2</sub> nanoparticles, and that the signal of Co was distinctly stronger than Ru, which was consistent with their different loading density.



Fig. 1. (a) TEM image of Ru/Co-TiO<sub>2</sub>. (b) HAADF-STEM image of Ru/Co-TiO<sub>2</sub>. Interplanar spacing of 0.35 nm corresponds to (101) planes of TiO<sub>2</sub>. No Co or Ru nanoparticles could be observed. (c) Elemental mapping of Ti, Co, and Ru in the Ru/Co-TiO<sub>2</sub> catalyst. Co and Ru could be observed sparsely dispersed on the surface of TiO<sub>2</sub> nanoparticles.

To further analyze the surface of the Ru/Co-TiO<sub>2</sub> catalyst, X-Ray Photoelectron Spectroscopy (XPS) investigations were carried out. Fig. S1a (Supporting information) shows the full survey XPS spectrum of the Ru/Co-TiO<sub>2</sub> catalyst. In the spectrum the peaks of Ti and O could be unambiguously observed, while the peaks of Ru and Co were not significantly visible. Due to the low content of Ru and the disturbance of Ti 2p peaks, the Ru 3p peaks could not be distinguished during fine scanning (Fig. S1b in Supporting information). Nevertheless, the Co 2p peaks in Fig. S1c (Supporting information) distinctly show that Co species in the catalyst had two oxidation states. The peaks at 786.0 eV and 801.7 eV corresponded to  $Co^{2+}$ , and the peaks at 780.9 eV and 796.4 eV corresponded to  $Co^{3+}$ . The

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analysis based on XPS investigation has further confirmed the low content of Ru and Co species in the Ru/Co-TiO<sub>2</sub> catalyst. In addition, the X-ray Diffraction (XRD) pattern in Fig. S2 (Supporting information) shows apparent diffraction peaks of Ru/Co-TiO<sub>2</sub> catalyst, while all of them belong to the planes of TiO<sub>2</sub>. No diffraction peaks associated to Ru or Co species could be observed, indicating the lack of related nanoparticles again.

The catalytic performance of the fabricated  $Ru/Co-TiO_2$  catalyst was evaluated with catalyzed  $NaBH_4$  hydrolysis under different conditions in a home-built setup [48]. The reaction mixtures of all hydrolysis reactions had the same total amount of 10 grams. In a typical experiment, 100 mg catalyst and 25 mg  $NaBH_4$  were mixed in an aqueous medium with 10 wt% NaOH to form 10 g reaction mixture to start the catalyzed hydrolysis, and the  $NaBH_4$  hydrolysis rate was reflected by the hydrogen generation (HG) rate. Various factors which influenced the hydrolysis rate including composition of catalysts, NaOH concentration,  $NaBH_4$  concentration, catalyst dosage and temperature were investigated in detail.

Aqueous solution of NaBH<sub>4</sub> is usually stabilized under alkaline conditions to prevent the unwanted self-hydrolysis. Therefore, a competent catalyst should have high activity for catalyzing NaBH<sub>4</sub> hydrolysis under alkaline conditions. In our study, we performed NaBH<sub>4</sub> hydrolysis experiments with different NaOH concentrations from 0 to 20 wt% (Fig. 2). It was found that NaBH<sub>4</sub> hydrolysis catalyzed by Ru/Co-TiO<sub>2</sub> had the highest HG rate of 10.34 mL/min when NaOH concentration was 10 wt%. Considering the loading density of Ru in the catalyst (0.06 wt%), the HG rate per gram Ru could be calculated to be 172 L min<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup>. This value is higher than the Ru efficiency of most recently reported Ru-based catalysts (Table S1 in Supporting information) [13-18,39-41]. If the average HG rate was calculated based on the amount of Co in the catalyst, it was 17 L min<sup>-1</sup> g<sub>Co</sub><sup>-1</sup>, which is also very high due to the contribution of Ru (Table S2 in Supporting information) [23-27].

When NaOH concentration was lower than 10 wt%, the existence of NaOH apparently accelerated the catalyzed NaBH<sub>4</sub> hydrolysis. However, when the concentration of NaOH was too high (higher than 10 wt%), the hydrolysis reaction became slower. It is widely accepted that the slowdown of the hydrolysis reaction when NaOH concentration was too high was caused by the increasing viscosity of the reaction mixture, but how low concentration of NaOH accelerated the catalyzed NaBH<sub>4</sub> hydrolysis is still unknown.

The Co-TiO<sub>2</sub> catalyst showed a similar trend as Ru/Co-TiO<sub>2</sub>, providing highest catalytic activity when NaOH concentration was 12.5 wt%. This is consistent with the results reported in previous studies [30,32,46]. However, Ru-TiO<sub>2</sub> showed a different trend. The HG rate of the reactions catalyzed by Ru-TiO<sub>2</sub> (3.65 mL/min) was on the same level with Ru/Co-TiO<sub>2</sub> (5.47 mL/min) when NaOH was absent. But the existence of NaOH had distinct inhibiting effect for Ru-TiO<sub>2</sub> catalyst. With the increasing of NaOH concentration, the NaBH<sub>4</sub> hydrolysis rate decreased dramatically. When NaOH concentration was above 12.5 wt%, hydrogen could hardly be produced.



Fig. 2. The HG rate of NaBH<sub>4</sub> hydrolysis catalyzed by Ru/Co-TiO<sub>2</sub>, Ru-TiO<sub>2</sub>, or Co-TiO<sub>2</sub> under different NaOH concentrations. Experimental conditions: 100 mg catalysts, 25 mg NaBH<sub>4</sub>, 30 °C.

To elucidate the impact of NaBH<sub>4</sub> concentration on the rate of hydrolysis catalyzed by Ru/Co-TiO<sub>2</sub>, experiments with different NaBH<sub>4</sub> concentrations were carried out. It could be concluded from Figs. 3a and b that the hydrolysis rate increased sharply when NaBH<sub>4</sub> concentration was increased from 0.10 wt% to 0.25 wt%, but deceased gradually when NaBH<sub>4</sub> concentration was further increased from 0.25 wt% to 10 wt%. As shown in Fig. 3a, when NaBH<sub>4</sub> concentration was higher than 0.25 wt%, hydrogen bubbles emerged as soon as the NaBH<sub>4</sub> solution was mixed with Ru/Co-TiO<sub>2</sub> catalyst. However, if NaBH<sub>4</sub> concentration decreased from 0.25 wt%, the initiation of the hydrolysis reaction gradually became more difficult, and therefore the volume of hydrogen generated at the very beginning was very little. Actually, in the catalyzed NaBH<sub>4</sub> hydrolysis experiments, we noticed that the colour of the Ru/Co-TiO<sub>2</sub> catalyst changed from grey to black during the reactions. When NaBH<sub>4</sub> concentration was low enough, it could be further observed that hydrogen bubbles could be generated in the solution only after the colour change of the catalyst had finished. This was consistent with the phenomenon reported by Demirci et al. in 2011 [49]. It indicates that the active form of the catalyst might not be the fresh prepared Ru/Co-TiO<sub>2</sub>, but be some product from Ru/Co-TiO<sub>2</sub> reacted with NaBH<sub>4</sub> solution. This is a very important point for the investigation on the potential mechanisms of NaBH<sub>4</sub> hydrolysis catalyzed by Ru/Co-TiO<sub>2</sub>. However, as emphasized by Demirci et al., the elucidation of the mechanisms will be a much tougher work to do [50]. Anyway, due to the lag phase at the beginning, the average hydrolysis rate of reactions decreased sharply as NaBH<sub>4</sub> concentration decreased from 0.25 wt% (Fig. 3b). However, when NaBH<sub>4</sub> concentration was increased from 0.25 wt%, the difference at the very beginning of the reactions became not distinguishable. On the contrary, with the increase of NaBH<sub>4</sub> concentration, the increase of solution viscosity and the formation of more NaBO<sub>2</sub> around the catalyst nanoparticles started to hinder mass exchange in

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the reaction [33,43,46]. As a result, the general hydrolysis rate gradually decreased (Fig. 3b). Nevertheless, although the increase of NaBH<sub>4</sub> concentration brought about acceleration or slowdown of hydrolysis reactions, the yield of hydrogen was not significantly affected. The final volume of hydrogen generated increased proportionally with the increasing of NaBH<sub>4</sub> concentration (Fig. S3 in Supporting information).

The change of dosage of the Ru/Co-TiO<sub>2</sub> catalyst dramatically affected NaBH<sub>4</sub> hydrolysis rate in another way. As shown in Figs. 3c and d, when the catalyst amount increased from 50 mg to 200 mg, the hydrolysis rate increased linearly from 4.60 mL/min to 20.06 mL/min, indicating that the catalyst was fully utilized in the hydrolysis reactions.



**Fig. 3.** (a and b) NaBH<sub>4</sub> hydrolysis under conditions with different NaBH<sub>4</sub> concentrations. (a) Plots of H<sub>2</sub> volume *versus* time for hydrolysis reactions with different NaBH<sub>4</sub> concentrations; Experimental conditions: 10 wt% NaOH, 100 mg Ru/Co-TiO<sub>2</sub>, 30 °C. (c and d) NaBH<sub>4</sub> hydrolysis under conditions with different Ru/Co-TiO<sub>2</sub> dosages. (c) Plots of H<sub>2</sub> volume *versus* time for hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>. (d) The HG rates of hydrolysis reactions catalyzed by different amount of Ru/Co-TiO<sub>2</sub>.

Temperature plays an important role in the NaBH<sub>4</sub> hydrolysis as it is an exothermic reaction. To investigate the temperature effects on our system, the reactions were carried out at 30 °C, 40 °C, 50 °C and 60 °C. As shown in Figs. 4a and b, the NaBH<sub>4</sub> hydrolysis rate increased sharply with the increasing of temperature. The HG rate of the hydrolysis reactions at 30 °C was just 10.34 mL/min, while it jumped to 45.54 mL/min when it was 60 °C, with 3.4 times increasing (Fig. 4b). Moreover, the activation energy (*E<sub>a</sub>*) of the hydrolysis reactions catalyzed by Ru/Co-TiO<sub>2</sub> was calculated with Arrhenius equation (Eq. (1)):  $\ln k = \ln A - E_a/RT$ 

where *T* is the reaction temperature of NaBH<sub>4</sub> hydrolysis in Kelvin (K), *k* is the rate constant of the hydrolysis reaction, *R* is the gas constant, and *A* is pre-exponential factor. Based on the NaBH<sub>4</sub> hydrolysis rates reflected by the HG rates at different temperatures, the  $E_a$  was calculated to be 38.74 kJ/mol (Fig. 4c), which is comparable with the  $E_a$  of NaBH<sub>4</sub> hydrolysis reactions catalyzed by other reported Ru-based catalysts (Table S1 in Supporting information) [13-17,39-41], demonstrating good catalytic activity of Ru/Co-TiO<sub>2</sub>.

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Fig. 4. (a-c) The impact of temperature on Ru/Co-TiO<sub>2</sub> catalyzed NaBH<sub>4</sub> hydrolysis. (a) Plots of H<sub>2</sub> volume versus time for hydrolysis reactions at different temperatures. (b) The HG rates of hydrolysis reactions catalyzed by Ru/Co-TiO2 at different temperatures. (c) Arrhenius plot for Ru/Co-TiO2 catalyzed NaBH4 hydrolysis; Experiment conditions: 10 wt% NaOH, 25 mg NaBH<sub>4</sub>, 100 mg Ru/Co-TiO<sub>2</sub>. (d) The durability of Ru/Co-TiO<sub>2</sub> in multi-cyclic NaBH<sub>4</sub> hydrolysis. Experimental conditions: 10 wt% NaOH, 25 mg NaBH<sub>4</sub>, 100 mg Ru/Co-TiO<sub>2</sub>, 30 °C.

To verify the practicability of  $Ru/Co-TiO_2$  in practical applications, the durability tests were carried out by evaluating the activity of catalyst in cycle use. After each use, the used catalyst was collected from the reaction mixture by centrifuging, washed with water, and dried in vacuum at 60 °C. And then it was used for catalyzing NaBH<sub>4</sub> hydrolysis again. As show in Fig. 4d, the NaBH<sub>4</sub> hydrolysis rate at the 5th cycle was 97.1% of the rate at 1st cycle. After the 5th experiment, the used catalyst was further characterized with high resolution TEM, XPS and XRD. The results (Fig. S4 in Supporting information) showed that no significant changes could be observed on the catalyst after being used for 5 cycles. It demonstrates that the Ru/Co-TiO<sub>2</sub> catalyst had excellent durability in catalyzing NaBH<sub>4</sub> hydrolysis.

In summary, a Ru/Co-TiO<sub>2</sub> catalyst composed of TiO<sub>2</sub> nanoparticles with Ru and Co species highly dispersed on the surface was developed by coprecipitation of  $Ru^{3+}$  and  $Co^{2+}$  on TiO<sub>2</sub> nanoparticles in aqua regia. The structures and chemical compositions of the Ru/Co-TiO<sub>2</sub> catalyst were verified with ICP-OES, TEM, HAADF-STEM, XPS, and XRD investigations. The experimental results showed that the Ru/Co-TiO<sub>2</sub> catalyst had superior performance for catalyzing NaBH<sub>4</sub> hydrolysis in the alkaline solution with 10 wt% NaOH, providing a hydrogen generation rate per gram Ru at 30 °C as high as 172 L min<sup>-1</sup> g<sub>Ru</sub><sup>-1</sup>, better than most of the previously reported Ru-based catalysts. Moreover, the Ru/Co-TiO<sub>2</sub> catalyst also showed excellent durability in cycle use, with just 2.9% of activity loss after being used for 5 times. These advantages made it a potential choice for catalyzing NaBH<sub>4</sub> hydrolysis to supply hydrogen in portable systems.

#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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