

## AN EFFICIENT TiO<sub>2</sub>-SUPPORTED RUTHENIUM (Ru/TiO<sub>2</sub>) CATALYST FOR ELECTROCHEMICAL HYDROGEN GENERATION FROM AQUEOUS POTASSIUM BOROHYDRIDE

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In this study, a TiO<sub>2</sub>-supported ruthenium catalyst (denoted as Ru/TiO<sub>2</sub>) was facilely synthesized by chemical reduction method without the use of any chemical reducing reagents. Using a 2 wt.% KBH<sub>4</sub> + 1 wt.% KOH solution, hydrogen generation rate was as high as 137423.9 mL\* min<sup>-1</sup> g<sup>-1</sup> at 30 °C, and apparent activation energy was calculated as 55.48 kJ\*mol<sup>-1</sup>. Compared with similar Ru-based catalysts reported in literature, the Ru/TiO<sub>2</sub> catalyst synthesized by chemical reduction method in this study indicates higher catalytic activity and lower apparent activation energy.

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### 1. Introduction

Proton exchange membrane fuel cell (PEMFC) is considered to be the most promising fuel cell technology for vehicular, stationary and portable application. But an efficient, safe and convenient hydrogen storage or supply system is still a problem to be solved for their commercialization [1, 2]. Recently, extensive research efforts have been devoted to the hydrogen generation via the hydrolysis of various chemical hydrides, such as NaBH<sub>4</sub> [3], NaAlH<sub>4</sub> [4], NH<sub>3</sub>BH<sub>4</sub> [5], and LiBH<sub>4</sub> [6] due to the high materials-only hydrogen storage gravimetric and volumetric efficiencies, and particularly to its easy generation of hydrogen for portable application at room temperature. In order to control the hydrogen generation from the hydrolysis reaction, the use of a catalyst plays an important role [7-9].

Up to now, few studies on hydrogen generation from hydrolysis of potassium borohydride (KBH<sub>4</sub>) have been found probably due to its low gravimetric density of hydrogen, slow kinetics and high production cost compared to NaBH<sub>4</sub> [10, 11]. However, KBH<sub>4</sub> has better hygroscopic properties than NaBH<sub>4</sub> and releases less heat during the hydrolysis process, which might be of importance for potential reactor design [12].

Hydrogen generation technology based on KBH<sub>4</sub> hydrolysis offers a practical means of meeting the requirements of portable fuel cell devices, distributed electricity supplies and even small-scale hydrogen refueling stations. However, the development and application of highly active catalysts remain an important aspect of commercializing this system [13, 14]. Noble-metal catalysts such as Pt [15], Pd [16], Ru [17], Au [18], Pd-Pt alloy [19] always present excellent catalytic performance for hydrogen generation. Among these catalysts, Ru-based ones are relatively low-cost and possess favorable activity and durability, resulting in a considerable investigation [17].

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TiO<sub>2</sub> is a typical semiconductor and electron-hole pairs can be generated on its surface by exposure to light irradiation. Theoretically, metal ions having a higher reduction potential than the conduction band value of semiconductor should be reduced by the excited electrons [20].

In our present study, Ru catalyst was deposited on the surface of TiO<sub>2</sub> support (denoted as Ru/TiO<sub>2</sub>) without the use of any chemical reducing reagents. Catalytic performance of the resulting Ru /TiO<sub>2</sub> catalyst was investigated and compared with other catalysts reported in the literature for KBH<sub>4</sub> hydrolysis to generate hydrogen.

## 2. Experimental part

Ru /TiO<sub>2</sub> catalysts were synthesized by in-situ reduction of metal salt (Ru) on the surface of TiO<sub>2</sub>. RuCl<sub>3</sub> was reduced by using KBH<sub>4</sub> and the TiO<sub>2</sub> particles were incorporated into the Ru-B alloy under the sonication. In order to control the rate of release of free metal ions for reaction, the citric acid was used as the complexing agent. Typically, 0.0045 g of RuCl<sub>3</sub> and 0.5 g of citric acid were dissolved in 10 mL of deionized water. About 0.2 g of nano-TiO<sub>2</sub> was then added to the solution and the solution was sonicated for 1 h at 50 °C. A freshly prepared 1 mL KBH<sub>4</sub> (0.00423 g) solution was then added dropwise into the above solution, also under sonication. After 1 h, the black precipitate was washed thoroughly with deionized water and absolute ethanol. Then the sample was left to dry in under vacuum at 60 °C for 24 h. For comparison, the Ru (0) catalyst was also synthesized under the same conditions.

Powder X-ray diffraction (XRD) patterns of Ru /TiO<sub>2</sub> catalyst sample were obtained with a D8 ADVANCE X-ray diffractometer using Cu K<sub>α</sub> radiation operating at 40 kV and 50 mA. The morphology and composition of the catalyst were investigated by scanning electron microscopy (SEM, JSM 6700 F, operating at 8 kV) and energy-dispersive spectroscopy (EDS, INCA Energy).

## 3. Results and discussion

### 3.1. Effect of TiO<sub>2</sub> loading on the hydrogen generation

Since the hydrogen generation of the hydrolysis is highly influenced by the doped materials, the effect of TiO<sub>2</sub> on the activity of the catalyst was investigated by changing the amount of TiO<sub>2</sub> in the Ru precursor solution. As shown in Figure 1, the hydrogen generation rate increased with the increasing amount of TiO<sub>2</sub> loaded, and it reached a maximum value at 2.5 wt.%. The hydrogen generation rate tended to decrease with further additions of TiO<sub>2</sub> in the catalyst. The explanation for this observation is thought to be that the surface of the TiO<sub>2</sub> supporting material was not completely coated by the Ru catalyst when too much TiO<sub>2</sub> was added. The optimized amount of TiO<sub>2</sub> for doping was thus found to be 2.5 wt.%, which was the amount chosen for the hydrolysis of KBH<sub>4</sub>.

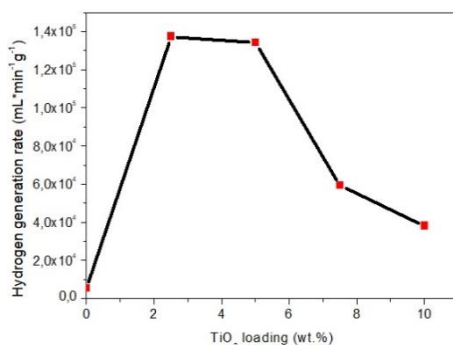


Fig. 1. Effect of different amounts of TiO<sub>2</sub> loading on the hydrogen generation rate.

### 3.2. Effect of $\text{KBH}_4$ concentration on hydrogen generation

It is obvious that a high  $\text{KBH}_4$  concentration can provide more hydrogen density. Figure 2 shows the effect of initial  $\text{KBH}_4$  on the hydrogen volume in the presence of  $\text{Ru}/\text{TiO}_2$  catalyst at  $30^\circ\text{C}$ . When  $\text{KBH}_4$  concentration increases from 1 to 6 wt.% the hydrogen volume increases significantly. However, in most cases, a higher  $\text{KBH}_4$  content in the alkaline solution for hydrogen production does not improve the generation rate. When the  $\text{KBH}_4$  concentrations are 1, 2, 4 and 6 wt.%, the hydrogen generation rates are measured to be 207415.6, 137423.9, 85831.2 and 82275.7  $\text{mL} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$ , respectively. This situation is reasonable because the reaction will consume more water and produce more hydrated byproduct at a higher  $\text{KBH}_4$  concentration, which can significantly increase the viscosity of the solution, thus hindering the mass-transport and decreasing the reaction rate. A similar phenomenon has been found on the hydrolysis of  $\text{NaBH}_4$  [21]. Also, the decrease of hydrogen generation rate with borohydride concentration was reported in some kinds of literature [22, 23].

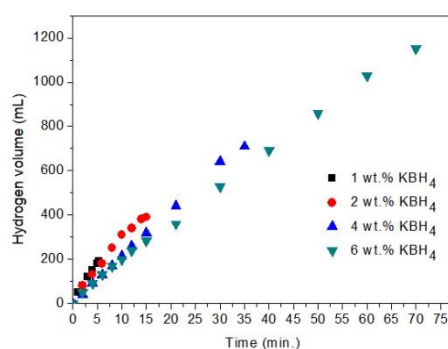


Fig. 2. Kinetic curves for hydrogen generation by hydrolysis of  $x$  wt.%  $\text{KBH}_4$  + 1 wt.%  $\text{KOH}$  solution ( $x = 1, 2, 4, 6$ ) at  $30^\circ\text{C}$ .

### 3.3. Effect of amount of catalyst on hydrogen generation

Fig. 3 indicates the hydrogen generation rate measured using the prepared  $\text{Ru}/\text{TiO}_2$  catalyst and 2 wt%  $\text{KBH}_4$  solution (10 mL) at  $30^\circ\text{C}$ . To examine the effects of catalyst loading on the hydrogen generation rate, 10, 20, 40 and 60 mg of the catalyst were employed. As observed in Figure 3, the reaction time required to complete the reaction decreased rapidly with increasing catalyst amount. Moreover, it was observed that the amount the hydrogen generation rate increased for the first a few minutes due to activation of the catalyst and then remained almost constant. Those results imply that hydrogen generation rate can be determined by controlling the catalyst loading used in the reactor.

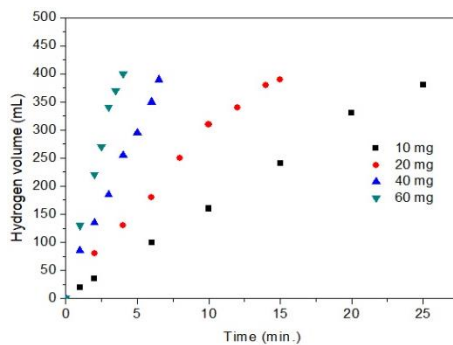


Fig. 3. Hydrogen generation volumes from 2 wt%  $\text{KBH}_4$  + 1 wt.%  $\text{KOH}$  solution (10 mL) at  $30^\circ\text{C}$  using different amounts of  $\text{Ru}/\text{TiO}_2$  catalyst.

### 3.4. Effect of temperature on the hydrogen generation

Kinetic studies at varied temperatures were further carried out using the optimized catalyst. Fig. 4 presents the hydrogen generation kinetic curves at a solution temperature ranging from 20 to 50 °C. To minimize the effect of temperature changes resulted by the exothermic hydrolysis reaction, this set of experiments was carried out using 2 wt.%  $\text{KBH}_4$  solution (10 mL). This measure allows the solution temperature to be controlled to within  $\pm 1$  °C during the reaction. As expected, the initial hydrogen generation rate increases significantly with temperature.

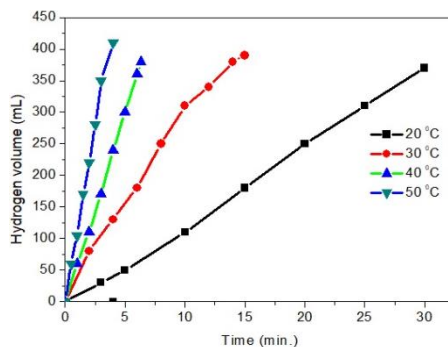


Fig. 4. Hydrogen generation volume as a function of reaction time with  $\text{Ru/TiO}_2$  catalyst measured at different temperatures by hydrolysis of 2 wt.%  $\text{KBH}_4$ + 1 wt.%  $\text{KOH}$  (10 mL) solution.

The influence of temperature is clearly shown by both the increasing slope values on the linear region of the plots and the decreasing induction period.

For comparison of catalysts activities, the initial hydrogen generation rates  $k$  ( $\text{mol} \cdot \text{min}^{-1} \text{g}^{-1}$ ) were used to determine the activation energy by the following Arrhenius equation:

$$\ln k = \ln k_0 - \left( \frac{E_a}{RT} \right)$$

where  $k_0$  is the rate constant ( $\text{mol} \cdot \text{min}^{-1} \text{g}^{-1}$ ),  $E_a$  the activation energy ( $\text{kJ} \cdot \text{mol}^{-1}$ ),  $R$  the gas constant ( $8.3143 \text{ kJ} \cdot \text{mol}^{-1} \text{K}^{-1}$ ), and  $T$  is the reaction temperature (K). An Arrhenius plot, in which  $\ln k$  is plotted against the reciprocal of absolute temperature ( $1/T$ ), was plotted in Fig. 5. From the slope of straight line, the activation energy was calculated to be  $55.48 \text{ kJ} \cdot \text{mol}^{-1}$ . This value compares favorably with the reported results for  $\text{Ru/graphite}$  ( $61.1 \text{ kJ} \cdot \text{mol}^{-1}$ ) [24]  $\text{Ru/LiCoO}_2$  ( $68.5 \text{ kJ} \cdot \text{mol}^{-1}$ ) [25] and  $\text{Ru/X-NW}$  ( $75 \text{ kJ} \cdot \text{mol}^{-1}$ ) [26] in literature.

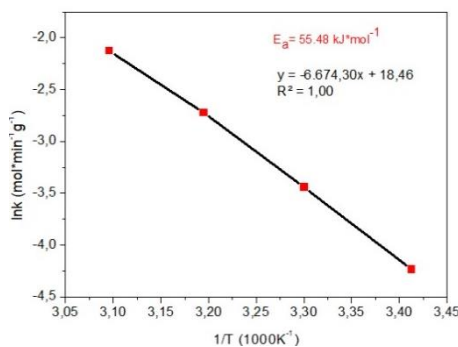


Fig. 5. Arrhenius plot obtained using the 2 wt.%  $\text{KBH}_4$ + 1 wt.%  $\text{KOH}$  solution (10 mL) and employing the  $\text{Ru/TiO}_2$  catalyst at different solution temperatures.

Table 1 presents various supported Ru-based catalysts, including their preparation methods and catalytic activities. The obtained results from the Table 1 shows that Ru/TiO<sub>2</sub> catalyst in this study exhibited a higher hydrogen generation rate than literature.

Table 1. Performance comparison between the prepared Ru/TiO<sub>2</sub> catalyst and literature results.

Catalyst	Preparation Method	Temperature (°C)	Hydrogen generation rate (mL* min <sup>-1</sup> g <sup>-1</sup> )	Reference
Ru/TiO <sub>2</sub> (NaBH <sub>4</sub> hydrolysis)	Photocatalytic reduction (PCR)	25	29600	[27]
Ru/TiO <sub>2</sub> (NaBH <sub>4</sub> hydrolysis)	Photocatalytic reduction (PCR)	30	38600	[27]
Ru/Graphite (NaBH <sub>4</sub> hydrolysis)	Impregnation reduction	30	32300	[28]
Ru-RuO <sub>2</sub> /C (NaBH <sub>4</sub> hydrolysis)	Galvanic replacement	50	16800	[29]
RuPt/LiCoO <sub>2</sub> (NaBH <sub>4</sub> hydrolysis)	Impregnation reduction	25	12400	[30]
Ru/TiO <sub>2</sub> (KBH <sub>4</sub> hydrolysis)	Impregnation chemical reduction	30	137423.9	This study
Ru/TiO <sub>2</sub> (KBH <sub>4</sub> hydrolysis)	Impregnation chemical reduction	50	378308.6	This study

### 3.5. Structural Properties of Ru/TiO<sub>2</sub> catalyst

The XRD patterns of Ru/TiO<sub>2</sub> catalyst are indicated in Fig. 6. It can be clearly seen from the Fig. 6 that diffraction peaks centered at 27.35<sup>o</sup>, 36.02<sup>o</sup>, 39.10<sup>o</sup>, 41.11<sup>o</sup>, 44.00<sup>o</sup>, 54.37<sup>o</sup>, 56.54<sup>o</sup>, 62.66<sup>o</sup>, 64.03<sup>o</sup> and 69.01<sup>o</sup> correspond to the crystallographic planes of (101), (103), (004), (111), (210), (105), (211), (204), (116) and (220) for TiO<sub>2</sub>, respectively (JCPDS card No. 65-5714). There are no characteristic peaks of metal Ru detected in the XRD pattern. It is reasonable that the Ru content is extremely low in the Ru/TiO<sub>2</sub> according to the EDS result will be shown in Fig. 8 and strong diffraction peaks of TiO<sub>2</sub> can easily cover the weak peaks of metal Ru.

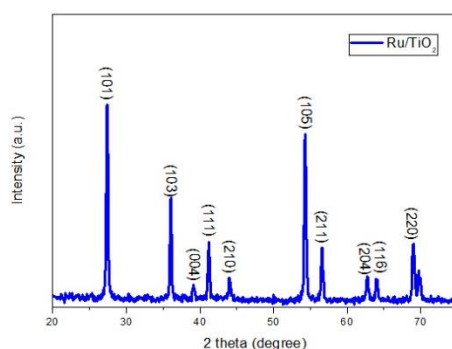


Fig. 6. XRD patterns of Ru/TiO<sub>2</sub> catalyst.

### 3.6. Morphological Properties and Elemental Analysis of Ru/TiO<sub>2</sub> catalyst

As a complement to this characterization, scanning electron microscopy (SEM, LEO 1430 VP) was utilized, so as to identify the microstructure and morphology of Ru/TiO<sub>2</sub> catalyst. SEM image and result of EDS analysis for Ru/TiO<sub>2</sub> catalyst are shown in Figure 7 and 8, respectively. Figure 7 shows that the prepared Ru/TiO<sub>2</sub> catalyst are spherical and well dispersed with average crystallite size of about 100 nm. EDX spectra of Ag-TiO<sub>2</sub> powders in Figure 8 demonstrates distribution of Ru, Ti and O components.

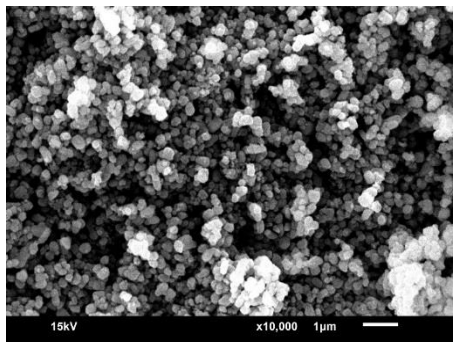


Fig. 7. A SEM image for Ru/TiO<sub>2</sub> catalyst.

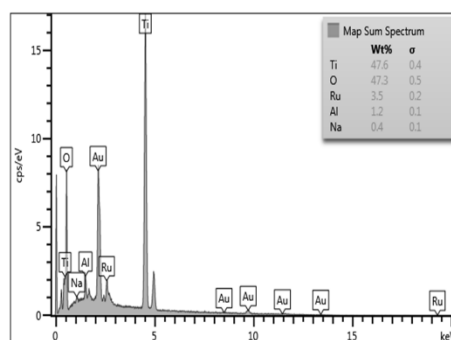


Fig. 8. EDX analysis and elemental mapping of Ru/TiO<sub>2</sub> catalyst.

## 4. Conclusions

In this study, a TiO<sub>2</sub>-supported ruthenium catalyst (denoted as Ru/TiO<sub>2</sub>) was facily synthesized by chemical reduction method without the use of any chemical reducing reagents. Using a 2 wt.% KBH<sub>4</sub> + 1 wt.% KOH solution, hydrogen generation rate was as high as 137423.9 mL\* min<sup>-1</sup> g<sup>-1</sup> at 30 °C, and apparent activation energy was calculated as 55.48 kJ\*mol<sup>-1</sup>. Compared with similar Ru-based catalysts reported in literature, the Ru/TiO<sub>2</sub> catalyst synthesized by chemical reduction method in this study indicates higher catalytic activity and lower apparent activation energy. Consequently, Ru/TiO<sub>2</sub> catalyst should be a significantly promising catalyst for commercial application of KBH<sub>4</sub> hydrolysis to generate hydrogen.

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