

Research Article

Hydrothermal Synthesis of Co-Ru Alloy Particle Catalysts for Hydrogen Generation from Sodium Borohydride

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Received 14 May 2013; Accepted 6 September 2013

Academic Editor: Hai Lu

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We report the synthesis of μm and sub- μm -sized Co, Ru, and Co-Ru alloy species by hydrothermal approach in the aqueous alkaline solutions ($\text{pH} \geq 13$) containing CoCl_2 and/or RuCl_3 , sodium citrate, and hydrazine hydrate and a study of their catalytic properties for hydrogen generation by hydrolysis of sodium borohydride solution. This way provides a simple platform for fabrication of the ball-shaped Co-Ru alloy catalysts containing up to 12 wt% Ru. Note that bimetallic Co-Ru alloy bowls containing even 7 at.% Ru have demonstrated catalytic properties that are comparable with the ones of pure Ru particles fabricated by the same method. This result is of great importance in view of the preparation of cost-efficient catalysts for hydrogen generation from borohydrides. The morphology and composition of fabricated catalyst particles have been characterized using scanning electron microscopy, energy dispersive X-ray diffraction, and inductively coupled plasma optical emission spectrometry.

1. Introduction

It is commonly accepted that borohydrides, due to high hydrogen density and low toxicity, are among the best hydrogen gas sources and storage containers. Note that hydrogen generation from sodium borohydride theoretically can attain 21.3 wt% if the by-product (water) is recycled for further hydrolysis. Furthermore, only pure H_2 gas and some water vapor are produced in the product gas stream through a chemical reaction of NaBH_4 or NH_4BH_4 with water according to an equation as follows:



Under SATP conditions only a small amount of hydrogen, depending on pH, is liberated from aqueous borohydride solutions [1, 2]. The generation rate, however, can be significantly increased if a suitable catalyst is applied [3, 4].

The first report on the hydrogen generation from borohydrides by hydrolysis and the accelerating effect of acids on the H_2 gas yield has been presented in the early 1950s [5]. A high efficiency of bulk ruthenium catalysts for hydrogen pro-

duction from borohydrides has been reported in several works [6–9]. As already referred, except for the transition metals and Ru, other precious metals such as Rh, Pd, and Pt and various metal oxides such as CoO , Co_3O_4 , TiO_2 , SiO_2 , NiO , LiNiO_3 , and LiCoO_2 can be successfully applied to catalyze the reaction (1) [10–13]. It has also been reported that decrease in the size of catalyst species results in the enhancement of hydrogen gas evolution rate [10], as it is typical for heterogeneous catalysis. By this way, Ru nanoparticles supported onto graphite [14] or a finely grained Ni catalysts [15] resulted in an exciting hydrogen generation rate increase. To date, various synthesis protocols have also been reported for fabrication of three-dimensional (3D) Co assembles composed of subunits such as nm-sized Co chains and Co sub-microspheres [16], Co nanoflowers, and nanorods [17], Co microspheres [18], and nanoflakes [19–22]. However, most of these hierarchical architectures have been created seeking to improve magnetic properties of nanostructured cobalt layers. The application of these materials for catalytic generation of hydrogen gas from borohydrides has not been reported yet. There are also no reports on the catalytic behavior of various

Co-Ru alloy species as catalysts for hydrogen generation from borohydrides. On the other hand, it is reasonable to suspect that bimetallic particles, possessing unique physical and chemical properties, allow them to be explored for efficient hydrogen generation. Therefore, the purpose of this study was to develop the synthesis protocols of Co, Ru, and Co-Ru bimetallic particles by a hydrothermal approach and to evaluate their efficiency as catalysts for sodium borohydride hydrolysis. In fact, the hydrothermal synthesis protocols of Co-Ru alloy submicrospheres, their morphology, and catalytic properties for hydrogen generation from borohydrides are explored here for the first time.

2. Experiments

All of the chemical reagents were of analytic grade purchased from Sigma-Aldrich and used without further purification. In a typical experimental procedure, 1.6 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 3.2 mmol Na citrate, and from 0 to 0.48 mmol RuCl_3 were dissolved in 30 mL distilled water. Following further addition of 1.0 to 3.0 mL of NaOH (5.0 M) solution and 4.8 mL of hydrazine hydrate (50%) and water up to the total volume of 40 mL, an alkaline solution containing 40 mmol/L of Co^{2+} ions with $\text{pH} \geq 13$ was obtained and sealed into an 80 mL Teflon-lined autoclave. The hydrothermal treatment was conducted at 120°C , using $10^\circ\text{C}/\text{min}$ ramp, for 10 h. The autoclave was then cooled to room temperature naturally. The products were harvested by centrifugation, thoroughly washed several times using distilled water and ethanol, and finally dried in an oven at 60°C . A similar procedure was performed following the synthesis of pure Ru species. In this case, a solution containing 40 mmol/L RuCl_3 , 80 mmol/L Na citrate, 0.125 mol/L NaOH, and 0.12 mol/L hydrazine hydrate was explored under the same hydrothermal conditions.

The composition of Co-Ru nanoalloys was studied directly by energy dispersive X-ray spectroscopy (EDX) and following dissolution of some quantity of synthesized products in a hot $\text{HNO}_3\text{-HCl}$ (1:3) solution by inductively coupled plasma optical emission spectrometry analysis.

The catalytic reactivity of synthesized Co, Ru, and Co-Ru alloy particles was determined by measuring the amount of hydrogen gas that evolved from the hydrolysis of sodium borohydride. To prevent self-hydrolysis, aqueous solutions containing 0.4% NaBH_4 were stabilized by addition of 0.25 mol/L NaOH. In each experiment, a freshly prepared solution (5.0 mL) was placed into a thermostated Erlenmeyer flash with the catalyst powder (5 mg) and sealed. The amount of generated hydrogen was determined with a volumetric burette in a gas analyzer every 2–5 min of processing.

Images of the particles were taken on a field emission scanning electron microscope (FESEM) model Hitachi S-6000. Samples were prepared by drying solvent dispersions of the nanoparticles onto the Formvar amorphous carbon-backed 200 mesh grid. X-ray powder diffraction experiments were performed on a D8 diffractometer (Bruker AXS, Germany), equipped with a Göbel mirror as a primary beam monochromator for CuK_α radiation.

The results are presented as the mean value of triplicate samples unless otherwise stated.

3. Results and Discussion

To generate the particles of Co, Ru, and various solid Ru solutions in Co we have used here degassed alkaline solutions composed of CoCl_2 and RuCl_3 precursors, NaOH, and hydrazine hydrate as a reducing agent. The complexation of these solutions was carried out through the addition of sodium citrate and NaOH up to $\text{pH} \geq 13.0$. It is noteworthy that in aqueous solutions the reduction potential of Co(II) species (-0.28 V) differs from Ru(III) ($+0.68\text{ V}$) significantly. Thence, the simultaneous reduction of cobalt and ruthenium species, possessing different reduction potentials, is somehow problematic. To overcome this, a strong reducer, particularly $\text{H}_4\text{N}_2 \cdot x\text{H}_2\text{O}$, and hydrothermal approach were applied in this study. We note that hydrothermal synthesis is a powerful tool embraces the chemical, thermal, and pressure induced driving forces allowing the formation of bimetallic crystalline materials from various precursors under appropriate treatment conditions [23].

Typical morphologies of the Co, Ru, and Co-Ru alloy products obtained under the optimized autoclaving conditions (120°C , 10 h, $10^\circ\text{C}/\text{min}$) are presented in Figure 1. As seen, fern-like cobalt species composed of numerous leaflets of up to several microns in length are formed in the solution without the ruthenium precursor (Figure 1(a)). Both the shape of metallic Co^0 species and sub- μm thickness of leaflets imply a huge surface area. The shape and size of pure Ru^0 species grown under the same autoclaving conditions differ significantly (Figure 1(b)). In this case, both separate spherical crystals of submicrometer size and the tangled ones forming spherical aggregates are formed. The morphology of bimetallic Co-Ru products produced by the same way was studied herein varying the concentrations ratio, $[\text{Co}^{2+}/\text{Ru}^{3+}]$, from 10:0.25 to 10:2 and the reaction temperature within the $[110\text{--}150]^\circ\text{C}$ range. In this way, we have found that increasing in $[\text{Ru}^{3+}]$ concentration results in the formation of Co-Ru species with a higher content of ruthenium attaining 12 wt%. Note that in most synthesis cases, the products obtained are bowl-shaped differing in size and dispersion of their diameters (Figure 1(c)). Besides, the surface of Co-Ru alloy bowls is not smooth and looks trenched (Figure 1(d)). It is also seen that some parts of Co-Ru dumplings, differing in size, are combined together implying that the growth of these crystallites proceeds via “oriented attachment” pathway by which nanoparticles with common crystallographic orientations combine [24].

To determine if Co-Ru particles could be generated in the same alkaline Co(II) and Ru(III) precursor solutions with sodium citrate at ambient pressure, control experiments at 20° , 40° , and 70°C were conducted. By this way, it was found that the reduction of cobalt and ruthenium species at room temperature proceeds exceptionally at a low rate without the formation of alloyed nanoparticles even during several days, while, at 40°C , Co-Ru alloy coats the glass-reactor walls just after several minutes (Figure 2(a)). The detailed observations

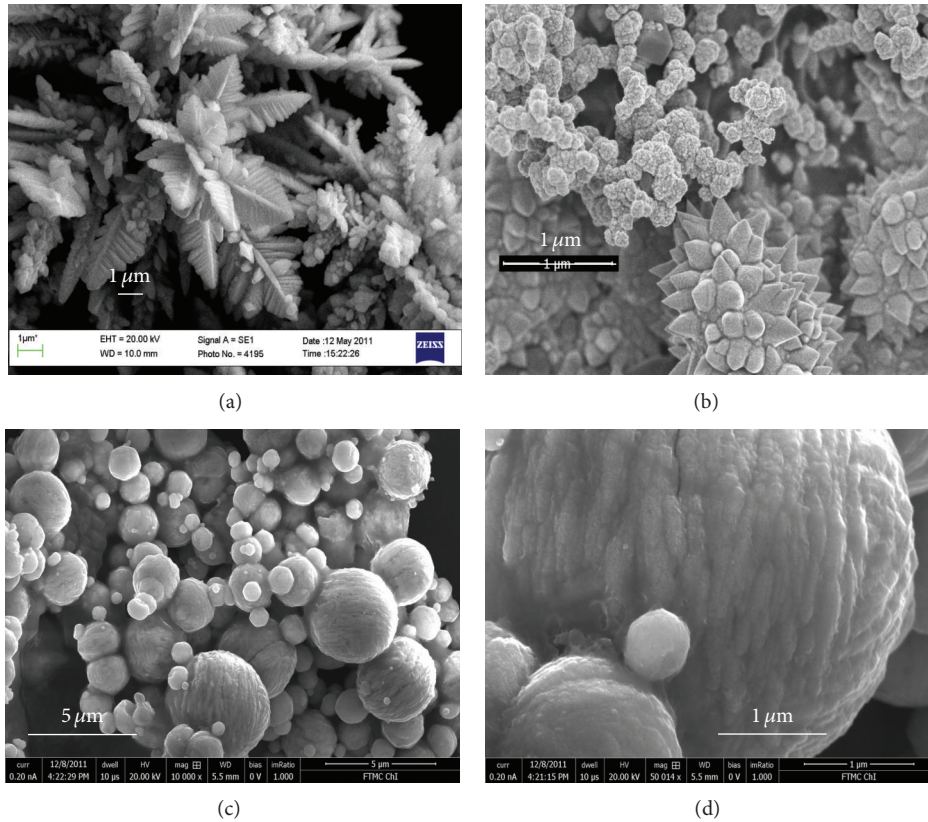


FIGURE 1: FESEM views of synthesized Co (a), Ru (b), and Co-Ru ((c), (d)) products by a hydrothermal way at 120°C for 10 h. The solution containing 0.04 CoCl_2 , 0.004 RuCl_3 , 0.08 sodium citrate, 0.33 NaOH , and 1.7 mol/L hydrazine hydrate was explored for Co-Ru fabrication, while for pure Co and Ru species, only their precursors at 0.04 mol/L and the same additives as for Co-Ru synthesis were used.

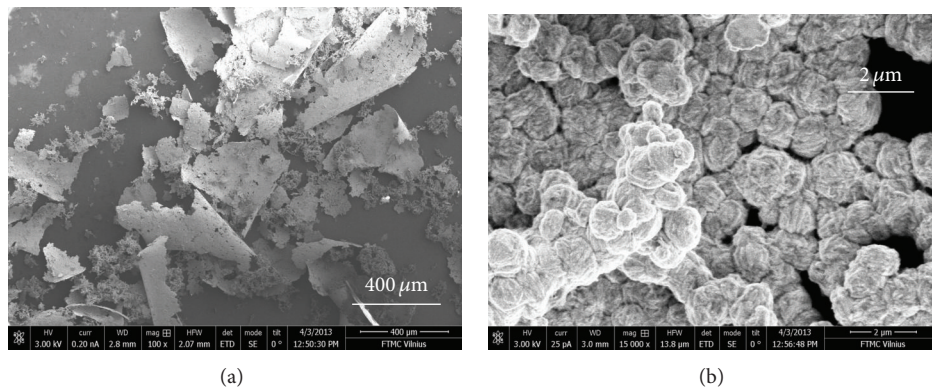


FIGURE 2: SEM views of Co-Ru alloy product formed in an aqueous solution of 0.04 CoCl_2 , 0.004 RuCl_3 , 0.08 sodium citrate, 0.33 NaOH , and 1.7 mol/L hydrazine hydrate at ambient pressure and 40°C for 5 min.

revealed that these films are composed of numerous micrometer-sized particles of Co-Ru alloy (Figure 2(b)). However, only 30 to 43% of ruthenium species were reduced under these conditions. Besides, the increase in the reaction temperature up to 70°C results into extremely intensive evolution of NH_3 gas and uncontrollable reaction directed to the formation of film material.

The XRD pattern (Figure 3(a)) of the Co-Ru alloy particles, obtained by autoclaving under conditions of this study

and containing up to 7 wt% of ruthenium, comprises six peaks at $2\theta = 41.15^\circ$, 44.34° , 46.88° , 61.80° , 75.03° , and 83.28° attributable to the hexagonal close-packed (*hcp*) space group $p63/mmc(194)$ of crystalline cobalt (PDF 01-071-4652) peaked at $2\theta = 41.44^\circ$, 44.08° , 47.22° , 62.10° , 75.58° , and 83.35° . A certain shift in experimental diffraction lines towards lower diffraction angles ought to be attributed to the formation of a solid solution of Ru in Co distorting the crystalline lattices of Co. The XRD pattern of Co-Ru alloy particles, containing

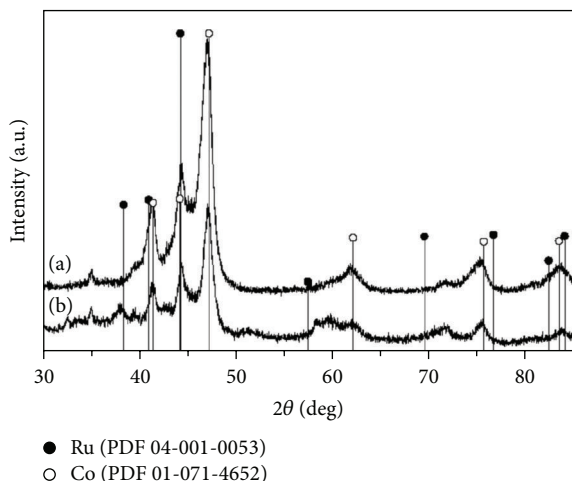


FIGURE 3: XRD patterns of species fabricated by hydrothermal route (120°C , 10 h) in the solutions containing 40 mmol/L CoCl_2 , 80 mmol/L sodium citrate, 0.33 mol/L NaOH, 108 mL/L hydrazine hydrate (50%), and RuCl_3 (mmol/L): (a) 2.5; (b) 5.0.

more Ru, is more complex (Figure 3(b)). Except the main diffraction peaks assigned to Co alloy, there are some weak additional peaks and shoulders, for example, at 2θ diffraction angles 35.01° and 71.53° . We suspect that in this case other finely grained crystalline phases in the solid solution of Ru in Co, such as $\text{Co}(\text{Co}_{1.108}\text{Ru}_{0.892})\text{O}_4$ indicated in PDF card no. 01-089-8629, could be formed.

As in the following, the hydrolysis of NaBH_4 solution was investigated by using synthesized Co, Ru, and Co-Ru alloy particles as catalysts. The plot in Figure 4 shows hydrogen production profiles for hydrolysis reaction (1) in a 5 mL solution containing 0.1 NaBH_4 + 0.25 mol/L NaOH + 5.0 mg of catalyst powder at a temperature of 30°C versus the processing time. It is seen that the highest hydrogen gas generation rate, approximated as $1.3 \text{ L}(\text{H}_2)/\text{min}\cdot\text{g}$, is characteristic for pure Ru^0 species, while under the same hydrolysis conditions the application of pure cobalt species gives only $0.18 \text{ L}(\text{H}_2)/\text{min}\cdot\text{g}$ yield. A quite high hydrogen generation rate for synthesized dendritically shaped Co species probably could be linked with a large surface area of this catalyst. From the numerous experimental results carried out in this study, the amount of evolved hydrogen under otherwise identical conditions was found to be dependent on the content of ruthenium in the catalysts increasing drastically with the Ru interposition. The effect of ruthenium content in the Co-Ru alloy on the hydrogen generation efficiency is obvious from the plot of the time spent for hydrolysis of half the amount of NaBH_4 ($t_{1/2\text{H}}$) presented in Figure 5. As seen, when 5 mg of the Co-Ru bowls containing only 7 at% of Ru was used as catalyst (inset in Figure 5) $t_{1/2\text{H}}$ approximated ≤ 3 min which is close to the time of hydrolysis of the same amount of NaBH_4 onto the pure 5 mg Ru catalyst (about 2 min), shown by a dashed line in Figure 5. These findings indicate that bimetallic Co-Ru sub- μM -sized bowls, synthesized by hydrothermal approach and containing only 5–7 at% of Ru, possess high catalytic activity and can be undoubtedly useful catalysts for the generation of hydrogen gas from borohydrides.

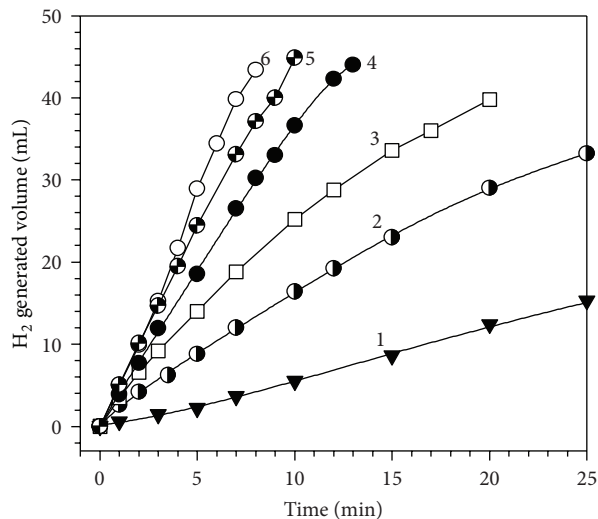


FIGURE 4: Volume of hydrogen generated from 5 mL of 0.1 NaBH_4 + 0.33 mol/L NaOH solution at 30°C as a function of processing time for synthesized Co (1), Ru (6), and Co-Ru alloy catalysts containing 2.6 (2), 3.8 (3), 5.7 (4), 7.1 (5), and 11.1 (6) at% Ru each in 5 mg.

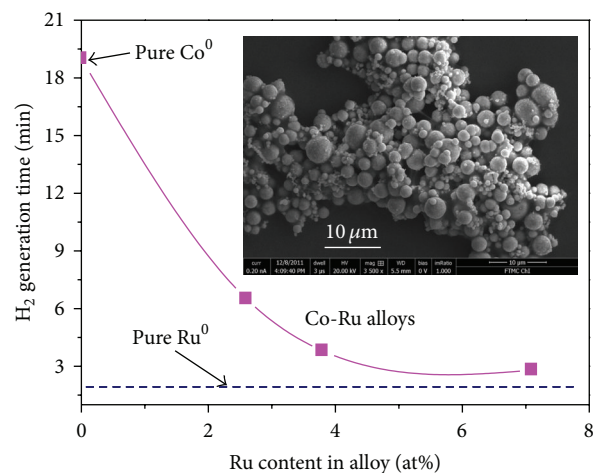


FIGURE 5: Variation of the time consumed for generation of half amount of H_2 gas from that theoretically calculated (47.4 mL) when 0.4% NaBH_4 solution (5 mL) was explored using 5 mg of pure Ru^0 (dashed line), pure Co, and Co-Ru alloy catalysts at 30°C . Inset depicts an FESEM view of alloy microspheres.

In this study, to determine the activation energy of NaBH_4 hydrolysis reaction on the Co-Ru alloy catalysts, H_2 generation rates were studied within the 20 to 60°C temperature range employing 5 mL of 0.1 NaBH_4 + 0.25 mol/L NaOH solution and 5 mg of powdered catalyst. The obtained kinetic plots for Co-Ru alloy (3.8 at% Ru) are presented in Figure 6(a). As seen, the increase in solution temperature results in increasing the rate of H_2 evolution. The hydrogen evolution rates determined at various processing temperatures were further

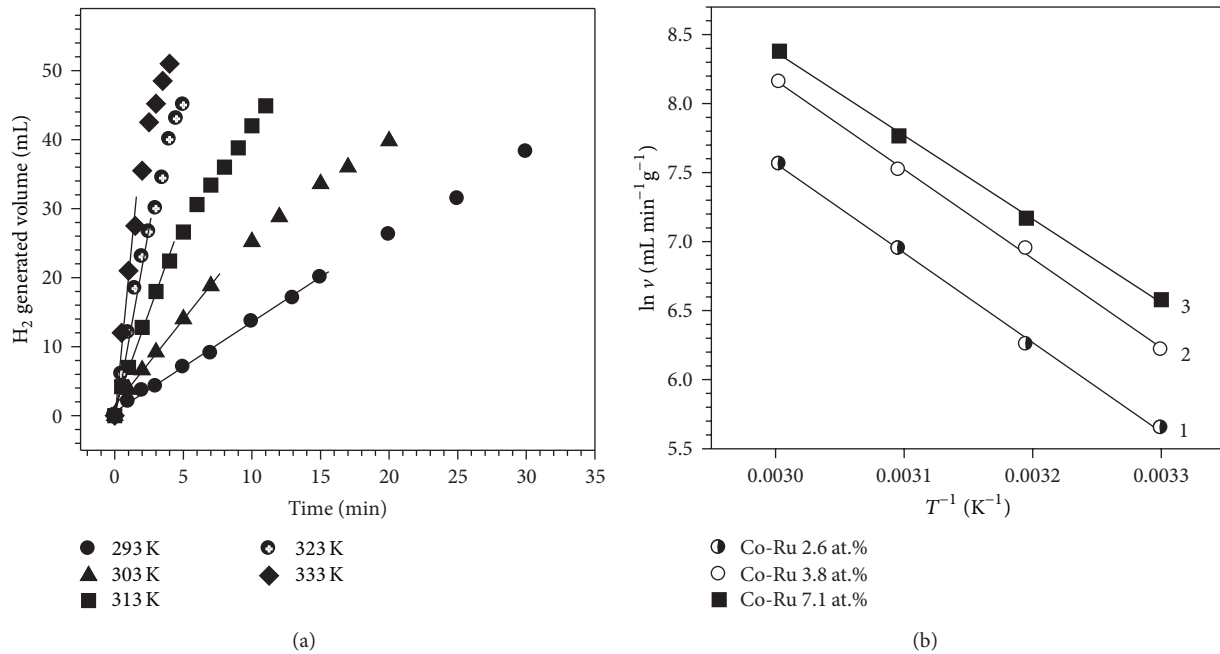


FIGURE 6: (a) Hydrogen generation kinetic plots of the 0.1 NaBH₄ + 0.25 mol/L NaOH solution employing the Co-Ru (3.8 at%) catalyst (5 mg) at indicated temperatures. (b) The Arrhenius plots calculated from NaBH₄ hydrolysis rates in the same solution for various Co-Ru alloy catalysts.

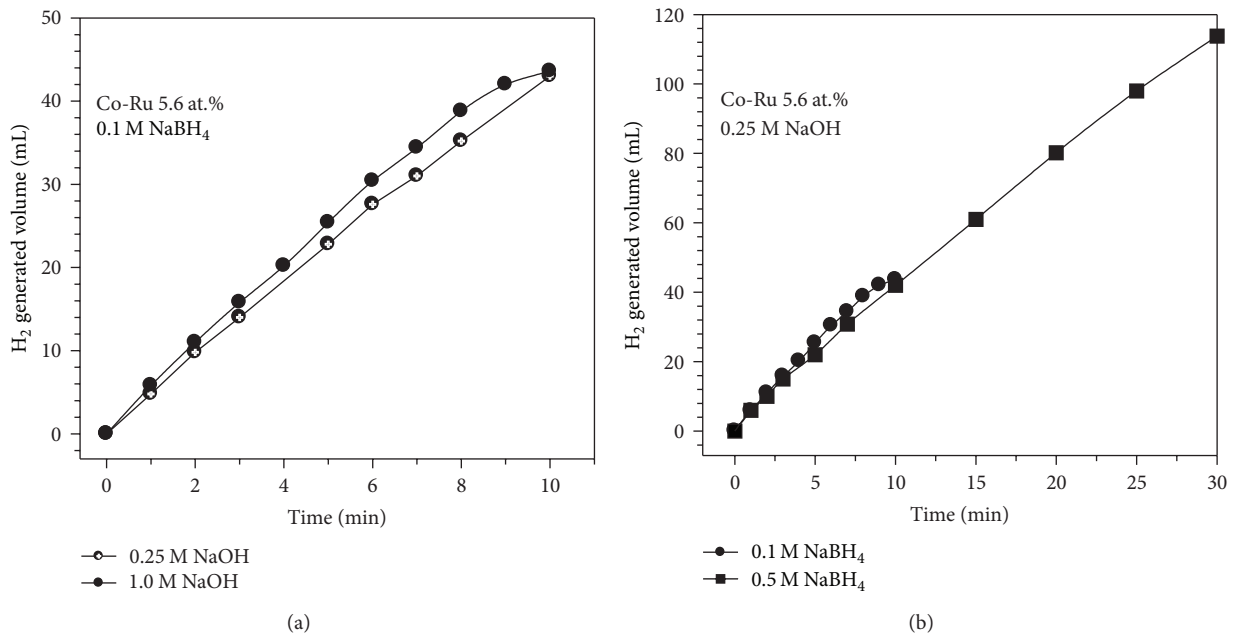


FIGURE 7: Volume of hydrogen generated as a function of time and the composition of solution applied for the Co-Ru (3.8 at%) catalyst.

applied to calculate the activation energy of various Co-Ru alloys according to the following relation:

$$v = k_0 \exp\left(-\frac{E_a}{RT}\right), \quad (2)$$

where v is the reaction rate in mL/min-g, k_0 is the reaction constant in mL/min-g, E_a is the activation energy of the

reaction (1) in kJ/mol, R is the gas constant (8.314 kJ/mol-K), and T is the reaction temperature in K. The calculated Arrhenius plots, for example, $\ln v$ versus $1/T$, for catalysts containing from 2.6 to 7.12 at% of Ru are shown in Figure 6(b). From the slopes of straight lines, the activation energy was approximated to be 53.5, 54.31 and 50.41 kJ/mol for Co-Ru microbowl catalysts containing 2.6, 3.8, and 7.1 at% of Ru,

respectively, which are higher than those of pure ruthenium nanoclusters (42 kJ/mol) [25] but significantly lower than those of bulk metallic Co (75 kJ/mol) [26].

It was reported that the concentration of NaOH can affect the rate of catalytic hydrolysis of NaBH₄: namely, inhibition characteristic of noble metal catalysts [8, 14, 27] and acceleration characteristic of transition metal catalysts [28–30]. The influence of NaOH concentration on H₂ generation rate for the Co-Ru alloy microsphere catalyst, fabricated in this study, is shown in Figure 7(a) which demonstrates a slight accelerating effect of [OH⁻] within at least a particular concentration range. However, variations in the concentration of NaBH₄ do not have a significant influence on the BH₄⁻ hydrolysis rate from the alkaline solution (Figure 7(b)), as in some other catalysts application cases [4, 31, 32].

4. Conclusions

In this work, for the synthesis of nanostructured Co-Ru alloy catalysts containing from several to 11 at% of Ru, an environmentally benign hydrothermal process in alkaline Co(II) and Ru(III) chloride solutions containing sodium citrate, NaOH and hydrazine hydrate has been suggested. Surprisingly, Co and Co-Ru alloy species of quite different structures have been obtained by this method under the same synthesis conditions without and with a RuCl₃ precursor. The addition of RuCl₃ to the reaction solution even in low concentrations results in the formation of bowl-shaped Co-Ru alloy particles instead of fern-like pure Co species traditionally formed without RuCl₃. It was also demonstrated that these Co-Ru bowls are effective catalysts for hydrogen generation from the alkaline solution of sodium borohydride. Note that hydrogen generation rates onto the Co-Ru alloy species containing only 5–7 at% of Ru are comparable to those obtained using pure Ru particles synthesized by the same approach.

Acknowledgments

The support of this work by the Lithuania Science Foundation under Grant no. ATE-08/2012 is gratefully acknowledged. The authors are grateful to Dr. V. Pakštas for help with XRD characterization.

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