

## Hydrogen Generation via Sodium Borohydride Hydrolysis Using Graphene Supported Platinum-Ruthenium-Cobalt Catalysts Prepared via Microwave-Assisted Synthesis

M. Semaško, L. Tamašauskaitė-Tamašiūnaitė, I. Stalnionienė, A. Žielienė, J. Vaičiūnienė, B. Šimkūnaitė-Stanyrienė, A. Selskis, and E. Norkus

Department of Catalysis, Center for Physical Sciences and Technology, Vilnius LT-01108, Lithuania

In this study the graphene supported PtRuCo catalysts were prepared with different Pt:Ru:Co molar ratios equal to 3.5:1:23, 1:1.7:5.6 and 1:2:2 by means of microwave synthesis. The shape and size of catalyst particles were examined using a Transmission Electron Microscopy. The catalytic activity of the graphene supported PtRuCo catalysts was evaluated with respect to the hydrolysis reaction of sodium borohydride by measuring the amount of generated hydrogen.

It was found that highest rates of hydrogen generation were obtained at 60 °C and are 53.1, 82.8 and 71.1 L min<sup>-1</sup> g<sup>-1</sup><sub>metal</sub> for the PtRuCo/GR catalysts with the Pt:Ru:Co molar ratios equal to 3.5:1:23, 1:1.7:5.6 and 1:2:2, respectively. The activation energy, determined from the kinetic data, is 50.2, 55.9 and 45.6 kJ mol<sup>-1</sup> for PtRuCo/GR with the above mentioned Pt:Ru:Co molar ratios, indicating a high catalytic activity of the synthesized catalysts towards hydrolysis of sodium borohydride.

### Introduction

Sodium borohydride is of interest as a source for a hydrogen generation during its catalytic hydrolysis (1). The development of catalysts with high activity with respect to the hydrolysis reaction of borohydride and durability plays an important role in the hydrogen generation for fuel cells. Non-noble catalysts such as Co (1-10) based catalysts, several ternary catalysts Co-X-B (X = Ni, P, Cr, Fe, Cu, Mo, W) (2, 11-21) and Ni (10, 22) as well as noble metal catalysts such as Pt (23,24), Ru (25-28) and Rh (29) have been developed for this purpose.

In the present study the graphene supported platinum-ruthenium-cobalt catalysts (denoted as PtRuCo/GR) were prepared by means of microwave-assisted synthesis as catalysts for hydrolysis of sodium borohydride. The PtRuCo/GR catalysts were prepared with different Pt:Ru:Co molar ratios. The shape and size of catalyst particles were examined using a Transmission Electron Microscopy (TEM). The composition of catalysts was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The catalytic activity of the graphene supported PtRuCo catalysts was evaluated with respect to the hydrolysis reaction of sodium borohydride.

## Experimental Procedure

The graphene supported PtRuCo catalysts (denoted as PtRuCo/GR) with the different Pt:Ru:Co molar ratios were prepared by means of microwave heating of  $\text{H}_2\text{PtCl}_6$ ,  $\text{RuCl}_3$  and  $\text{CoCl}_2$  in ethylene glycol (EG) solutions. Briefly, 0.25 ml of 0.0974 M  $\text{H}_2\text{PtCl}_6$ , 0.6 ml of 0.4 M  $\text{CoCl}_2$ , 0.125, 0.625, 1.25 ml of 0.0964 M  $\text{RuCl}_3$ , 0.8 ml of 1 M NaOH and 0.1 g graphene were mixed with 18.2 ml of EG and sonicated for 30 min. Then, the reaction mixture was put into a microwave reactor Monowave 300 (Anton Paar). The synthesis of catalysts was carried out at a temperature of 170°C for 30 min. After preparation, the synthesized catalysts were washed with acetone, ultra-pure water with the resistivity of  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ , then filtered and dried in a vacuum oven at 80 °C for 2 h. For comparison, the Co/GR and CoRu/GR catalysts were also synthesized under the same conditions. The shape and size of catalyst particles were examined using a transmission electron microscope Tecnai G2 F20 X-TWIN equipped with an EDAX spectrometer with an r-TEM detector. For microscopic examinations, 10 mg of sample were first sonicated in 1 ml of ethanol for 1 h and then deposited on a Cu grid covered with a continuous carbon film. The composition of the PtRuCo/GR, Co/GR and RuCo/GR catalysts was estimated using an ICP optical emission spectrometer Optima 7000DV (Perkin Elmer).

The catalytic activity of the graphene supported PtRuCo catalysts was evaluated with respect to the hydrolysis reaction of sodium borohydride by measuring the amount of generated hydrogen. The amount of generated hydrogen was measured by using MilliGascounter (Ritter). In a typical measurement, the 15 ml reaction solution containing 5 w%  $\text{NaBH}_4$  and 0.4 w% NaOH was thermostated in an airtight flask fitted with an outlet for collection of evolved  $\text{H}_2$  gas, connected with MilliGascounter. Then the 5 mg of different PtRuCo/GR, Co/GR and RuCo/GR catalysts in glass scoop were added into the solution with designated temperature to initiate hydrolysis reaction of sodium borohydride. Hydrogen generation rate was measured at different solution temperatures (30, 40, 50 and 60 °C) in order to determine the activation energy.

## Results and Discussion

In this study the graphene supported PtRuCo catalysts were prepared by means of microwave synthesis. It should be noted that the amounts of Pt and Co were kept constant, whereas the amounts of Ru were different. The composition of prepared catalysts was determined by Inductively Coupled Plasma Optical Emission Spectroscopy and is given in Table I.

**TABLE I.** Composition of the Co/GR, CoRu/GR and different PtRuCo/GR catalysts determined by ICP-OES.

Catalyst	Composition of catalyst (5 mg)			$M_{\text{metal}}$ , mg	Molar ratio of Pt:Ru:Co
	Pt	Ru	Co		
Co/GR	-	-	0.53	0.53	-
CoRu/GR	-	0.02	0.54	0.56	-
PtRuCo/GR	0.20	0.03	0.40	0.63	3.5:1:23
	0.18	0.17	0.33	0.68	1:1.7:5.6
	0.13	0.13	0.09	0.35	1:2:2

After the microwave heating of the reaction mixture at 170 °C for 30 min, the graphene supported PtRuCo catalysts were prepared with different Pt:Ru:Co molar ratios equal to 3.5:1:23, 1:1.7:5.6 and 1:2:2. The prepared catalysts were denoted as PtRuCo(3.5:1:23)/GR, PtRuCo(1:1.7:5.6) and PtRuCo(1:2:2).

Figure 1 presents TEM views of the prepared PtRuCo/GR catalysts with Pt:Ru:Co equal to 3.5:1:23 (a), 1:1.7:5.6 (b) and 1:2:2 (c).

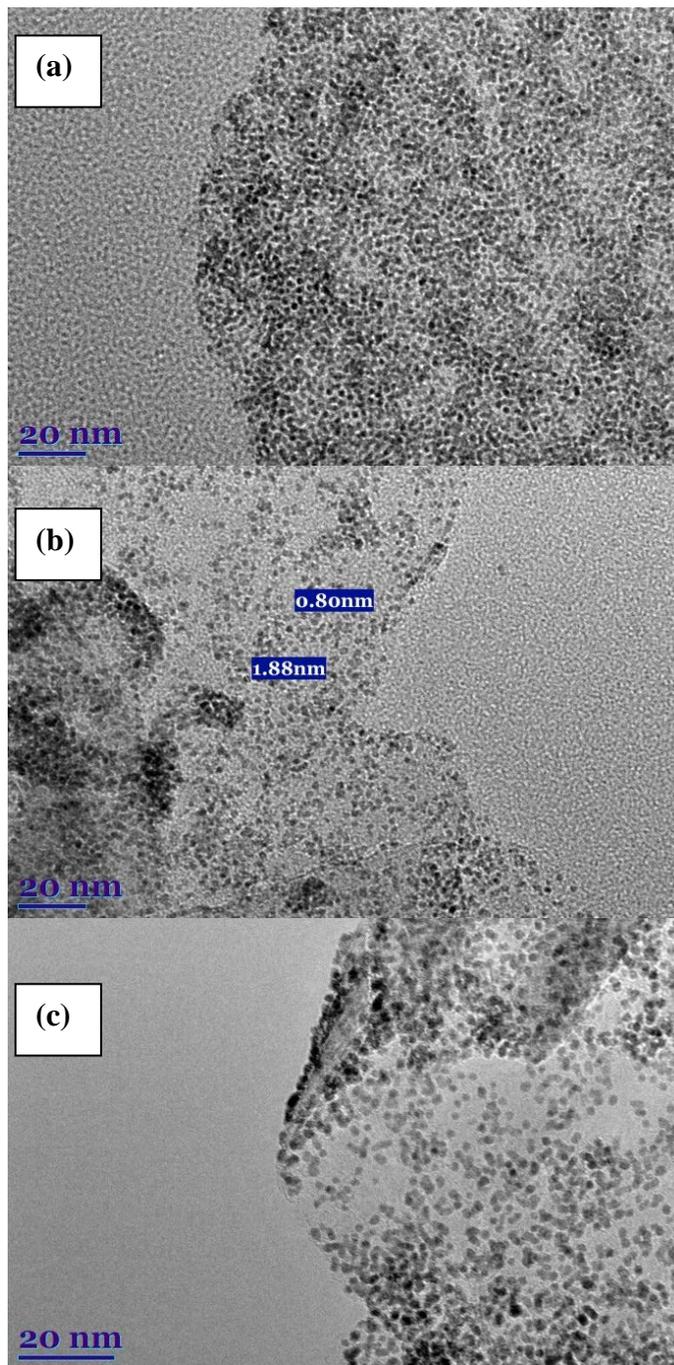


Figure 1. TEM views of PtRuCo(3.5:1:23)/GR (a), PtRuCo(1:1.7:5.6) (b) and PtRuCo(1:2:2) (c) prepared by microwave synthesis.

It was found that the PtRuCo/GR catalysts were synthesized with particle size of 1-3 nm.

The activity of the prepared Co/GR, CoRu/GR and PtRuCo/GR with different Pt:Ru:Co molar ratios catalysts was investigated towards the catalytic hydrolysis of  $\text{NaBH}_4$  at various temperatures. Figure 2 presents hydrogen generation rate measured during the hydrolysis of alkaline  $\text{NaBH}_4$  solution (5 w%  $\text{NaBH}_4$  + 0.4 w%  $\text{NaOH}$ ) using the Co/GR (a) and CoRu/GR (c) catalysts as a function of reaction temperature (30-60 °C).

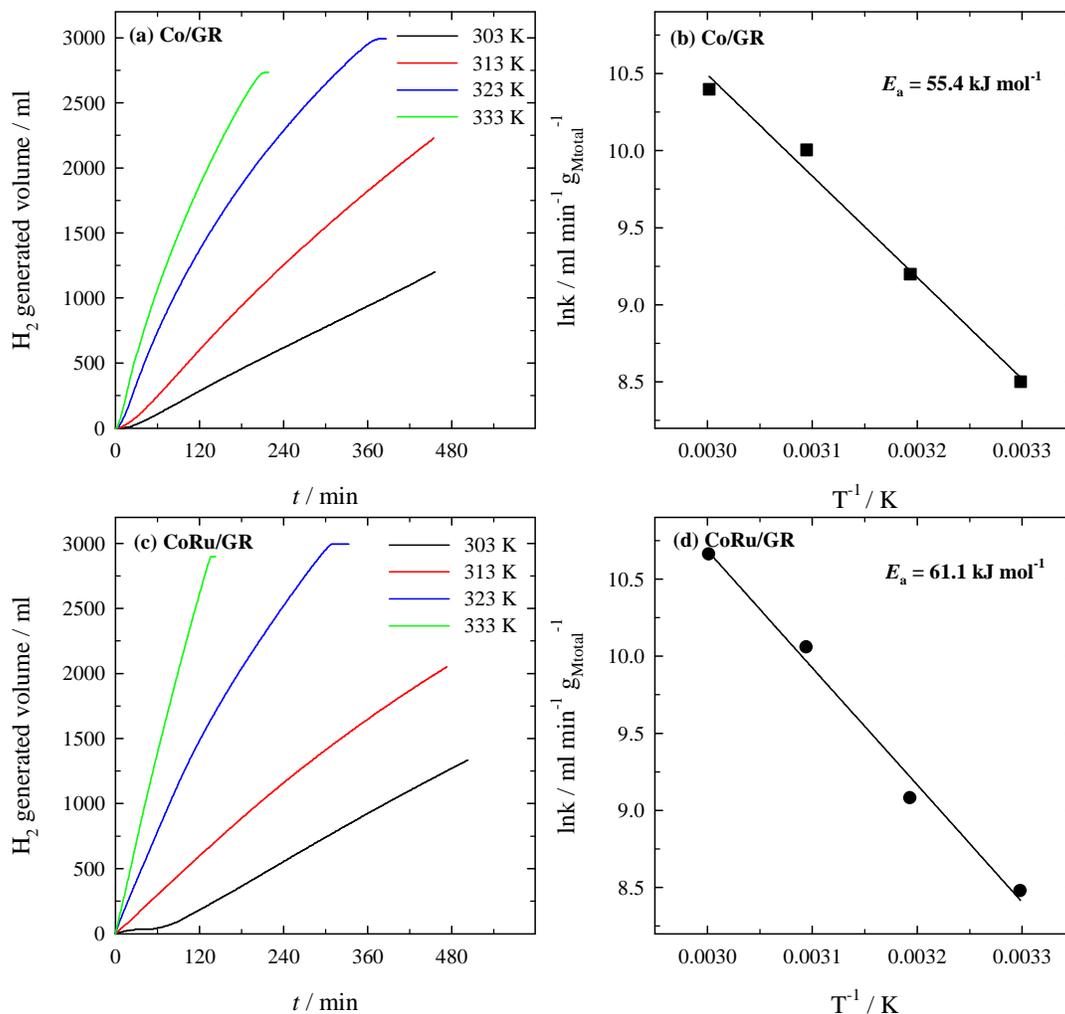


Figure 2.  $\text{H}_2$  generation from 15 ml 5 w%  $\text{NaBH}_4$  + 0.4 w%  $\text{NaOH}$  at a different solution temperature catalyzed by the Co/GR (a) and CoRu/GR (c) catalysts. (b, d) The Arrhenius plot calculated from the rates of  $\text{NaBH}_4$  hydrolysis in a same solution.

As well-known, temperature dependence of the rate of generation of hydrogen is expressed by the Arrhenius equation (30):

$$k = A e^{-E_a/RT}, \quad [1]$$

where  $E_a$  is the activation energy (J), A - the frequency factor, R - the general gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). In order to find activation energy and frequency factor, the Arrhenius plot of  $\ln(k)$  vs  $1/T$  was constructed from the data presented in Figs. 2 a and c and is given in Figs. 2 b and d. The Arrhenius plot gives activation energy of 55.4 and 61.1  $\text{kJ mol}^{-1}$  for the Co/GR and CoRu/GR, respectively (Figs. 2 b and d).

Hydrogen generation rate measured on the different PtRuCo/GR catalysts at temperatures of 30-60 °C is presented in Figs. 3 a-c. The Arrhenius plot calculated from the rates of  $\text{NaBH}_4$  hydrolysis for those catalysts is shown in Fig. 3d. The Arrhenius plot gives activation energy of 50.2, 55.9 and 45.6  $\text{kJ mol}^{-1}$  for the PtRuCo(3.5:1:23)/GR, PtRuCo(1:1.7:5.6)/GR and PtRuCo(1:2:2)/GR, respectively. Those values obtained on the PtRuCo(3.5:1:23)/GR, PtRuCo(1:1.7:5.6)/GR and PtRuCo(1:2:2)/GR catalysts are slightly higher than that obtained on Co ( $41.9 \text{ kJ mol}^{-1}$ ) and Raney Co ( $53.7 \text{ kJ mol}^{-1}$ ) (10).

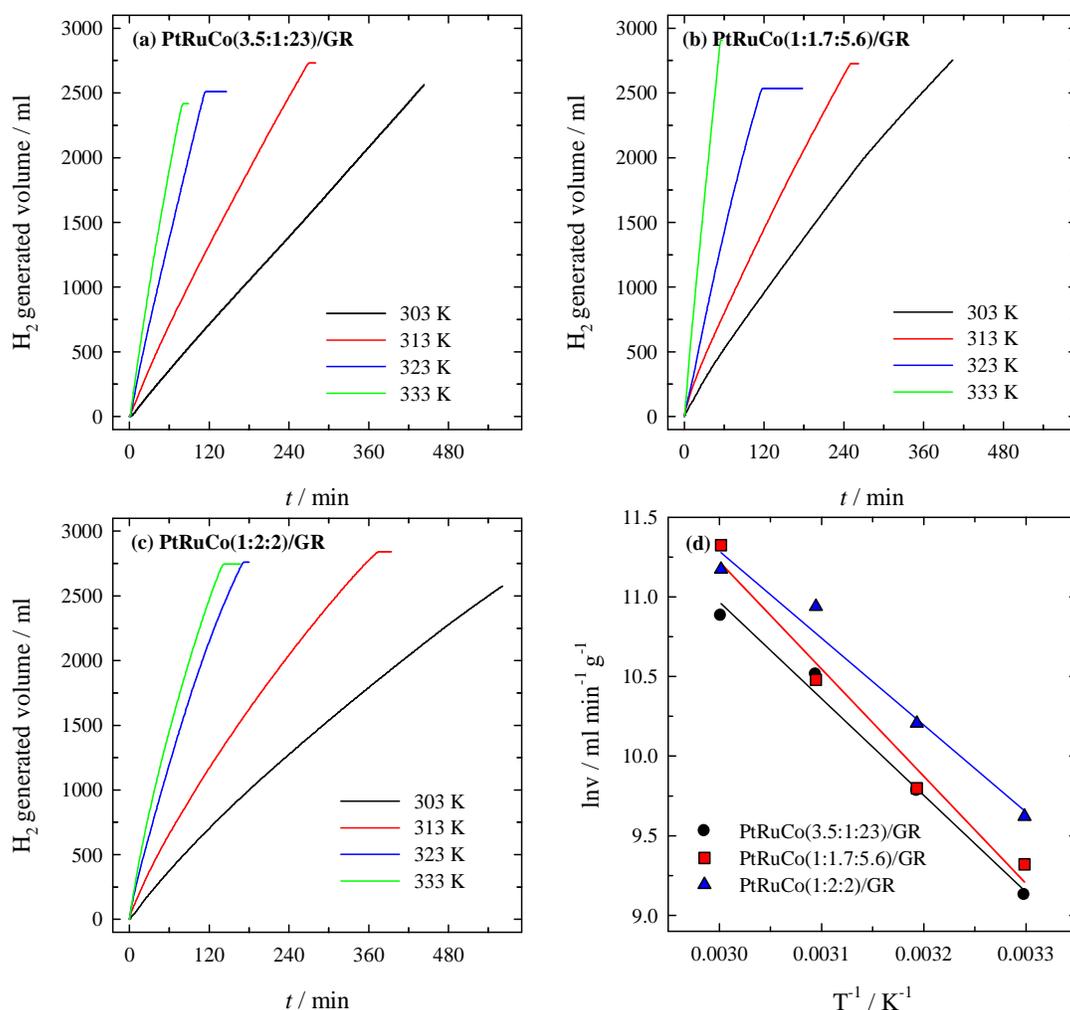


Figure 3.  $\text{H}_2$  generation from 15 ml 5 w%  $\text{NaBH}_4$  + 0.4 w% NaOH at a different solution temperature catalyzed by the PtRuCo(3.5:1:23)/GR (a), PtRuCo(1:1.7:5.6)/GR (b) and PtRuCo(1:2:2)/GR (c) catalysts. (d) The Arrhenius plot calculated from the rates of  $\text{NaBH}_4$  hydrolysis in a same solution.

In all cases, the rate of catalytic hydrolysis of  $\text{NaBH}_4$  in alkaline solutions increases exponentially with increase in reaction temperature as evident from Figs. 2 and 3. The data obtained are given in Table II. It should be noted that greater hydrogen generation rate is obtained at the synthesized PtRuCo/GR catalysts as compared with that at Co/GR and CoRu/GR.

**TABLE I.** Hydrogen generation rate obtained at Co/GR, CoRu/GR and PtRuCo/GR from 5 w%  $\text{NaBH}_4$  + 0.4 w% NaOH.

Catalyst	Temperature, K	$\text{H}_2$ generation rate, $\text{ml min}^{-1} \text{g}^{-1}_{\text{metal}}$	Activation energy, $\text{kJ mol}^{-1}$
Co/GR	303	4923	55.4
	313	9879	
	323	22126	
	333	32787	
CoRu/GR	303	4555	61.1
	313	8309	
	323	22094	
	333	40401	
PtRuCo(3.5:1:23)/GR	303	9201	50.2
	313	17700	
	323	36744	
	333	53108	
PtRuCo(1:1.7:5.6)/GR	303	11158	55.9
	313	17994	
	323	35524	
	333	82801	
PtRuCo(1:2:2)/GR	303	15082	45.6
	313	27050	
	323	56284	
	333	71145	

Figure 4 shows comparison of hydrogen generation rate obtained at the investigated catalysts from 5 w%  $\text{NaBH}_4$  + 0.4 w% NaOH at 60 °C.

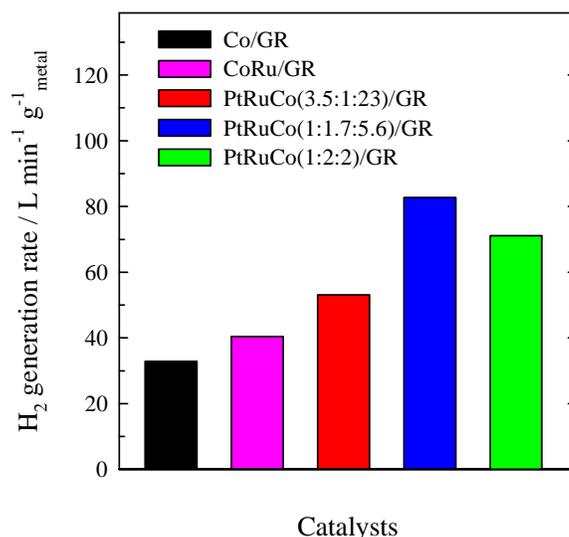


Figure 4.  $\text{H}_2$  generation rate obtained at Co/GR, CoRu/GR and PtRuCo/GR from 5 w%  $\text{NaBH}_4$  + 0.4 w% NaOH at 60 °C.

Highest rates of hydrogen generation were obtained at 60 °C and are 53.1, 82.8 and 71.1 L min<sup>-1</sup> g<sup>-1</sup><sub>metal</sub> for the PtRuCo/GR catalysts with the Pt:Ru:Co molar ratios equal to 3.5:1:23, 1:1.7:5.6 and 1:2:2, respectively (Table II, Fig. 4).

Therefore, the data obtained confirm that the graphene supported PtRuCo catalysts catalyzes efficiently the hydrolysis reaction of NaBH<sub>4</sub> in alkaline solutions.

### Conclusions

In this study the graphene supported PtRuCo catalysts were prepared with different Pt:Ru:Co molar ratios equal to 3.5:1:23, 1:1.7:5.6 and 1:2:2 by means of microwave synthesis. Greater hydrogen generation rate is obtained at the synthesized PtRuCo/GR catalysts as compared with that at Co/GR and CoRu/GR. Highest rates of hydrogen generation were obtained at 60 °C and are 53.1, 82.8 and 71.1 L min<sup>-1</sup> g<sup>-1</sup><sub>metal</sub> for the PtRuCo/GR catalysts with the Pt:Ru:Co molar ratios equal 3.5:1:23, 1:1.7:5.6 and 1:2:2, respectively. The activation energy, determined from the kinetic data, is 50.2, 55.9 and 45.6 kJ mol<sup>-1</sup> for PtRuCo/GR with the above mentioned Pt:Ru:Co molar ratios, indicating a high catalytic activity of the synthesized catalysts towards hydrolysis of sodium borohydride.

### References

1. S. S. Muir and X. Yao, *Int. J. Hydrogen Energy*, **36**, 5983 (2011).
2. H. B. Dai, Y. Liang, P. Wang, and H. M. Cheng, *J. Power Sources*, **177**, 17 (2008).
3. B. H. Liu and Q. Li, *Int. J. Hydrogen Energy*, **33**, 7385 (2008).
4. J. Lee, K. Y. Kong, C. R. Jung, E. Cho, S. P. Yoon, J. Han, T. G. Lee, and S. W. Nam, *Catal. Today*, **120**, 305 (2007).
5. Z. J. Wu, W. Li, M. H. Zhang, and K. Y. Tao, *Front. Chem. Eng. China*, **1**, 87 (2007).
6. Y. Huang, Y. Wang, R. Zhao, P. K. Shen, and Z. Wei, *Int. J. Hydrogen Energy*, **33**, 7110 (2008).
7. Z. J. Wu, J. S. Zhao, M. H. Zhang, W. Li, and K. Y. Tao, *Catal. Commun.*, **11**, 973 (2010).
8. J. Delmas, L. Laversenne, I. Rougeaux, P. Capron, A. Garron, S. Bennici, D. Swierczynski, and A. Auroux, *Int. J. Hydrogen Energy*, **36**, 2145 (2011).
9. C. C. Yang, M. S. Chen, and Y. W. Chen, *Int. J. Hydrogen Energy*, **36**, 1418 (2011).
10. B. H. Liu, Z. P. Li, and S. Suda, *J. Alloys Compd.*, **415**, 288 (2006).
11. Y. Liang, P. Wang, and H. B. Dai, *J. Alloys Compd.*, **491**, 359 (2010).
12. N. Patel, R. Fernandes, and A. Miotello, *J. Catal.*, **271**, 315 (2010).
13. M. Rakap, E. E. Kalu, and S. Ozkar, *J. Alloys Compd.*, **509**, 7016 (2011).
14. X. L. Ding, X. Yuan, C. Jia, and Z. F. Ma, *Int. J. Hydrogen Energy*, **35**, 11077 (2010).
15. J. C. Ingersoll, N. Mani, J. C. Thenmozhiyal, and A. Muthaiah, *J. Power Sources*, **173**, 450 (2007).

16. H. Li, Y. Wu, J. Zhang, W. Dai, and M. Qiao, *Appl. Catal. A: General*, **275**, 199 (2004).
17. H. B. Dai, Y. Liang, P. Wang, X. D. Yao, T. Rufford, M. Lu, and H. M. Cheng, *Int. J. Hydrogen Energy*, **33**, 4405 (2008)
18. R. Fernandes, N. Patel, A. Miotello, and M. Filippi, *J. Molec. Catal. A: Chem.*, **298**, 1 (2009).
19. N. Patel, R. Fernandes, and A. Miotello, *J. Power Sources*, **188**, 411 (2009).
20. R. Fernandes, N. Patel, and A. Miotello, *Appl. Catal. B: Environ.*, **92**, 68 (2009).
21. X. Yuan, C. Jia, X.-L. Ding, and Z.-F. Ma, *Int. J. Hydrogen Energy*, **37**, 995 (2012).
22. H. Dong, H.X. Yang, X. P. Ai, and C. S. Cha, *Int. J. Hydrogen Energy*, **28**, 1095 (2003).
23. Y. Kojima, K. Suzuki, K. Fukumoto, Y. Kawai, M. Kimbara, H. Nakanishi, and S. Matsumoto, *J. Power Sources*, **125**, 22 (2004).
24. M. Sankir, L. Semiz, R. B. Serin, and N. D. Sankir, *Int. J. Hydrogen Energy*, **40**, 8522, (2015).
25. S. C. Amendola, S. L. Sharp-Goldman, M. S. Janjua, M. T. Kelly, P. J. Petillo, and M. Binder, *J. Power Sources*, **85**, 186 (2000).
26. J. S. Zhang, W. N. Delgass, T. S. Fisher, and J. P. Gore, *J. Power Sources*, **164**, 772 (2007).
27. C.-L. Hsueh, C.-Y. Chen, J.-R. Ku, S.-F. Tsai, Y.-Y. Hsu, F. Tsau, and M.-S. Jeng, *J. Power Sources*, **177**, 485 (2008).
28. Y. Liang, H. B. Dai, L. P. Ma, P. Wang, and H. M. Cheng, *Int. J. Hydrogen Energy*, **35**, 3023 (2010).
29. Y. V. Larichev, O. V. Netskina, O. V. Komova, and V. I. Simagina, *Int. J. Hydrogen Energy*, **35**, 6501 (2010).
30. S. A. Arrhenius, *Z. Physik. Chem.*, **4**, 96 (1889).