Hydrogen generation from hydrolysis of sodium borohydride using Ni-Ru nanocomposite as catalysts[1]

Cheng-Hong Liu[a], Bing-Hung Chen[a,*], Chan-Li Hsueh[b], Jie-Ren Ku[b], Ming-Shan Jeng[b], Fanghei Tsau[b]

[a]*Department of Chemical Engineering, National Cheng Kung University, Tainan City, 701 Taiwan*

[b]*New Energy Technology Division, Energy and Environment Research Laboratories,*
Industrial Technology Research Institute, Hsinchu County, 310 Taiwan

Abstract

Magnetic Ni-Ru/50WX8 catalysts are synthesized with combined methods of conventional chemical reduction method and electroless deposition. Catalysts can be easily recycled with magnets owing to their intrinsic ferromagnetism. Thus, it is convenient to separate catalysts from spent $NaBH_4$ solution for further recycling. Effect of temperature on catalyst performance is less significant at higher temperature, which is beneficial to devices without good regulations on temperature. A rate of hydrogen evolution as high as 150 ml min^{-1} g^{-1} could be reached at 25°C, which, equivalently, can generate 15 W of power through a PEMFC. Different variables that affect the rate of hydrogen production are investigated. Activation energy of hydrogen generation using such catalysts is estimated at about 52.73 kJ mol^{-1}.

Keyword: hydrogen generation, catalyst, sodium borohydride, nickel, ruthenium.

Introduction

Renewable energy has attracted so much attention due to the ever-growing demands in friendly environment, especially with the increase of population and green-house gas emissions in the world. In addition, efficient sources of power for on-board energy generation on personal electronic products are required, too. The proton-exchange membrane fuel cell (PEMFC) is a promising attractive alternative power source because of its high energy conversion efficiency. However, its demand on high purity of hydrogen is of the major concern, along with the problem that such a PEMFC system could be dysfunctional because of poisoned catalyst in presence of impurities [1]. Consequently, hydrogen generated from steam reforming of natural gas, the common industrial process to produce hydrogen gas, is not suitable for feed to PEMFC devices due to inevitable poisoning of proton exchange membrane owing to the byproducts of this process, such as carbon monoxide.

For portable applications, high gravimetric and volumetric density of hydrogen storage is of the major concern to the success of such applications. Among various hydrogen storage systems, chemical hydrides are candidates with the greatest potentials in success, in terms of the low operation pressure, less cost and less energy losses. Moreover, the hydrogen content existing in

---

[1] This report contains results to be submitted for publication in academic journals.

* Corresponding author. Contact information: Tel.: +886–6–275–7575 Ext. 62695; Fax: +886–6–234–4496;
E-mail address: bkchen@mail.ncku.edu.tw (Bing-Hung Chen)

chemical hydrides is much higher than that of metal hydrides, which could possibly meet the goal of 9 wt% by 2015, declared by the U.S. Department of Energy (DOE) [2]. Among these chemical hydrides, sodium borohydride ($NaBH_4$) is one of the promising compounds, which is relatively safer because of its non-flammability and higher hydrogen content (10.8 wt%). In addition, $NaBH_4$ is stable in air and in alkaline solutions. An empirical relationship on stability of $NaBH_4$ with pH values of solutions and storage temperature [3] could be represented by

$$\log t_{1/2} = A_{pH} - (0.034 \cdot T - 1.92) \tag{1}$$

where $t_{1/2}$ is the half-life of self hydrolysis of $NaBH_4$ in minutes at a particular temperature T in K and in a solution with a pH value equal to A_{pH} in the absence of catalysts. That is to say, alkaline $NaBH_4$ solution at pH 14 can be kept for 430 days from self-decaying at room temperature.

Kaufman and Sen [4] utilized various acids to catalyze the hydrolysis of $NaBH_4$. They found that conversion efficiency over 90% could be achieved with oxalic acid in 10 minutes. Besides, hydrogen can be released via the addition of suitable catalysts, which is shown as followed [5]:

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} NaBO_2 + 4H_2 + 217kJ \tag{2}$$

In presence of appropriate catalysts, the hydrolysis reaction of $NaBH_4$ can be easily started or terminated. Even more, the rate of hydrogen generation can also be well-controlled. Furthermore, the recycle of spent-$NaBH_4$ has already been studied and reported by other authors using different methods [6-8], which can effectively lower the cost of $NaBH_4$ production such as to increase its popularity in usage by humans.

As catalysts play such a vital role in hydrogen evolution from hydrolysis of $NaBH_4$, numerous substances have been attempted to be efficacious in increasing the rate of hydrogen evolution but not in lowering the controllability of hydrogen generation. These catalysts include precious metals, such as Ru and Pt, as well as alloys, like Pt-Ru alloys, on various supports [9-11]. From our previous work, Ru catalysts supported on ion-exchange resin were successfully synthesized by a simple chemical reduction method to catalyze the hydrolysis of $NaBH_4$ solution for hydrogen generation [12]. In the viewpoint of cost saving, non-noble metal catalysts like cobalt and nickel should be developed in replacement of Pt and Ru [13, 14].

In this study, magnetic catalysts of nickel-ruthenium supported on polymers (Ni-Ru/50WX8) were developed not only to accelerate the hydrogen release from hydrolysis of $NaBH_4$, but also to lower down the operation cost in recycling the spent $NaBH_4$ modules. The intrinsic ferromagnetic property of catalyst is beneficial for the easy recycling process of catalyst from spent $NaBH_4$ by using proper permanent magnets. In addition, the surface morphology as well as compositions of the catalysts were also investigated and are discussed. It is found that a rate of hydrogen evolution as high as 150 ml min^{-1} g^{-1} could be reached at 25°C, which, equivalently, can generate 15 W of power through a proper PEMFC and enough for many personal electric products. Moreover, effects of $NaBH_4$ and NaOH concentration as well as process temperature on rate of hydrogen production were summarized in this report.

2. Experimental

2.1 Preparation of Ni-Ru/50WX8 catalysts

All the reagents were of analytical grade and used without further purification. Strong acid exchange resin beads, Dowex 50WX8 in hydrogen form and of 50 ~ 100 mesh size, used for catalyst supports with sulfonic acid as active functional groups were purchased from Dow Chemicals. Properties of Dowex 50WX8 were given in details in Table 1.

Weighted amounts of Dowex 50WX8 resin beads were placed into $RuCl_3$ solution of desired concentration at the ambient temperature to start the chelating reaction. After 1 hour of uniformly stirring, Dowex 50WX8 resins chelated with ruthenium ion, referred as Ru^{3+}/50WX8, were taken out and washed with deionized water repeatedly to remove any possible residual Ru^{3+} unchelated to the surface of Dowex 50WX8. Ru^{3+}/50WX8 particles added into appropriate amounts of deionized water were preheated to 70°C. Vigorous reduction reaction of Ru^{3+} was initiated by addition of overdosed $NaBH_4$ as a reducing reagent. Consequently, Ru^{3+} on the surface of Dowex 50WX8 was reduced to Ru giving the Ru-polymer complex, called Ru/50WX8.

To facilitate the electroless nickel deposition on Ru/50WX8, electroless Ni bath was prepared by dissolving suitable amount of $NiCl_2$, $Na_3C_6H_5O_7$ and maleic acid in deionized water, followed by adjusting pH value to 9.5 with NaOH. The composition of electroless Ni bath in details along with the plating conditions were given in Table 2. After preheating electroless Ni bath to 80°C, 2.5 ml of N_2H_4 as a reducing reagent for the electroless nickel process and Ru/50WX8 resins were poured in order into the bath solution to initiate the electroless reaction. After 60 minutes, the electroless deposition process was terminated by cooling down the bath temperature. The resulted nickel-ruthenium-Dowex WX8 complexes were taken out by magnet for repeated cleansing by deionized water. The Ni-Ru/50WX8 catalysts were synthesized by further doping aforementioned Ni-Ru-Dowex WX8 complexes with Ru in similar method mentioned above. The formulation of electroless Ru solution and plating conditions were also given in Table 2. After carefully cleansing surface of as-prepared Ni-Ru/50WX8 catalysts with deionized water, catalysts were dried in vacuum at 60°C to remove any left-over water on these Ni-Ru/50WX8 catalysts.

2.2 Surface characterization of Ni-Ru/50WX8 catalysts

The morphology of the prepared Ni-Ru/50WX8 catalysts was identified by using a scanning electron microscope (SEM; JEOL JSM-6700F), whereas the elemental compositions on catalyst surfaces were analyzed with the energy dispersive spectra (EDS) from an Oxford INCA-400 spectrometer installed on this SEM.

2.3 Generation of hydrogen

2.3.1 Batch observation of hydrogen production

The rate and the volume of H_2 evolved in presence of Ni-Ru/50WX8 catalysts were measured by utilizing a conventional water-displacement way, which was described in details along with its experimental setup in our previous report [12]. 15 ml of $NaBH_4$ solution containing appropriate concentration of NaOH were thermostatically kept in a sealed flask at the preset temperature using thermostatic circulator in which the water temperature was kept constant within 0.1°C from the set value. The onset of the H_2 generation reaction was defined as one minute from the moment when a fixed amount, *ca.* 200 mg, of Ni-Ru/50WX8 catalysts was introduced into the flask containing the $NaBH_4$ alkaline solution. One minute was assumed sufficiently for catalysts to be moistened with $NaBH_4$ solution. An outlet tube connecting the flask was placed under an inverted water-filled burette, which was situated in a graduated cylinder filled with water. The volume of hydrogen released was measured by observing water displaced from the graduated glass column as the reaction proceeding.

2.3.2 Continuous measurement of hydrogen release

Continuous generation rate of hydrogen from $NaBH_4$ hydrolysis was monitored. 15 ml of $NaBH_4$ solution with appropriate NaOH concentration was prepared in a funnel equipped with a pressure-equalization at one of the openings of the three-necked round-bottom flask. One of the flask openings was connected to a continuous mass flow meter (MFM) and the other one to a thermometer. 200 mg of Ni-Ru/50WX8 catalysts were added in the flask as the reactor, which was subsequently preheated to the desired temperature by using thermostatic circulator having good temperature controllability within 0.1°C. The reaction was initiated when pouring $NaBH_4$ solution into the flask. The whole H_2 production process was monitored by the MFM.

3. Results and discussion

3.1 Characterization of Ni-Ru/50WX8 catalysts

The major factor that affects the rate of hydrolysis for $NaBH_4$ is the activity of catalysts utilized. Hence, identification of properties and surface morphology of the catalysts are necessary. Figure 1 shows the EDS analyses, which depict the composition of Dowex 50WX8 resin beads and Ni-Ru/50WX8 catalysts that were synthesized for hydrogen generation. Apparent peaks representing Ru and Ni were observed at around 2.7 keV and 1 keV, respectively, in Figure 1(b). However, it is of note that existence of Pt element on both samples comes from sputtered Pt on both samples prior to SEM/EDS analysis to increase the electric conductivity on the surfaces of both samples. Interestingly, sulfur element appeared, as sulfonic groups as active sites are present on the surface of Dowex 50WX8 resin beads.

Surface compositions of Ni-Ru/50WX8 catalysts are listed in details in Table 3. It is found that 17.0 at% (or 8.0 wt%) of Ni and 37.4 at% (or 10.4 wt%) of Ru were detected, whereas other elements, such as C, O and S, obviously decrease to 19.3 wt%, 16.8 wt%, and 9.2 wt%, respectively, compared to the pristine Dowex resin supports, owing to partial coverage with Ru and Ni on catalyst surface.

SEM images depicting surface morphologies of original Dowex 50WX8 resin beads and Ni-Ru/50WX8 catalysts are shown at various magnifications (Figure 2). The average size of the resin beads is approximate to 200 μm (Figure 2(a)). Moreover, surface of the original resin beads is quite smooth, even being observed at a higher magnification (50,000×) as shown in Figure 2(e). After Ni and Ru were deposited on to the surface of Dowex 50WX8 resin beads by ion exchange and electroless deposition, surface of the Ni-Ru/50WX8 catalysts does not show obvious difference under lower magnification (500×). However, the terrain of the Ni-Ru/50WX8 is quite rugged under observation at higher magnifications (10,000×; 50,000×). In addition to the growth of Ru and Ni catalysts on the surface of resin beads, the surface area must have also increased due to the rough morphology.

3.2 Generation of hydrogen

In general, rate of hydrogen production is mainly dependent on the activities of the catalysts. However, other factors, such as the $NaBH_4$ concentration, alkaline conditions and process temperature, could still play significant roles in the hydrolysis of $NaBH_4$. These factors were studied and will be discussed in next section.

3.2.1 Effect of NaOH concentration

Figure 3 shows the variation of hydrogen generation rate with different NaOH concentration in 5 wt% $NaBH_4$ solution at 25°C in presence of 200 mg Ni-Ru/50WX8 catalysts. The rate of hydrogen evolution increases from 115 to 125 ml min^{-1} g^{-1}, as NaOH concentration rises from 1 to 5 wt%, and decreases to 81 ml min^{-1} g^{-1} with a further increase in NaOH concentration up to 15 wt%. Similar trends on hydrogen evolution were reported by Ingersoll et al. [14], who utilized Ni-Co-B catalysts for hydrolysis of $NaBH_4$ in presence of various NaOH concentrations. They have arrived as well at an optimum NaOH concentration around 15 wt% due to the nature of the catalysts used. Ye et al. [15] also obtained similar results by adopting $Co/\gamma\text{-}Al_2O_3$ as catalysts to generate hydrogen gas from $NaBH_4$ but did not give a further explanation on an optimum NaOH concentration of 10 wt% they garnered. With our conjecture, it is possible that too much OH^- anions generated with an increasing NaOH concentration in the solution will compete with the transfer of BH_4^- anion, so that the surfaces of catalysts in the system could be significantly occupied by OH^- rather than BH_4^- anions. That is, BH_4^- anions available on catalyst surface to generate hydrogen is reduced and so is the rate of hydrogen evolution.

4. Conclusion

Magnetic Ni-Ru/50WX8 catalysts utilized to produce hydrogen from hydrolysis of $NaBH_4$ were synthesized by combined methods of chemical reduction and electroless deposition. Great convenience in recycle of these catalysts can be achieved due to the intrinsic ferromagnetic property of Ni-Ru/50WX8 catalysts. Hence, catalysts could be easily separated from spent $NaBH_4$ solution using permanent magnets in this recycle process. Factors, such as process temperature, and concentrations of NaOH and $NaBH_4$ that affect the rate of hydrogen evolution, were studied. An optimal condition in hydrogen generation was found in a system containing 10 wt% of $NaBH_4$ in 5 wt% NaOH, which gives a maximum rate of hydrogen generation near 150 ml min^{-1} g^{-1}. Equivalently, such a hydrogen production rate can generate 15 W by using a proper PEMFC device commonly available. Steady hydrogen release was observed under the aid of a mass flow meter (MFM). In general, over 90% of hydrogen conversion is reached in presence of various $NaBH_4$

concentrations. From the temperature-dependent relationship of the H_2 generation rates, the activation energy in such a catalyst-assisted H_2 production process is 52.73 kJ mol^{-1}.

Acknowledgement

The work was financially supported by the Bureau of Energy of the Ministry of Economic Affairs of the Republic of China (Taiwan) under Contract No. 7455DC5220.

Reference

[1] J.J. Baschuk, X. Li, Int. J. Energy Res. 25 (2001) 695-713.

[2] B. Tumas, in 2007 Annual Merit Review Proceedings – Hydrogen Storage, "*DOE Chemical Hydrogen Storage Center of Excellence Overview*", (May, 2007).

[3] M.M. Krevoy, R.W Jacobson, Ventron Alembic. 15 (1979) 2-3.

[4] C.M. Kaufman, B, Sen, J. Chem. Soc. Dalton. Trans. (1985) 307-313.

[5]H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hoekstra, E.K. Hyde, J. Am. Chem. Soc. 75 (1953) 215-219.

[6] C.H. Hale, H. Sharifian, US Patent 4,931,154 (1990).

[7] Z.P. Li, N. Morigazaki, B.H. Liu, S. Suda, J. Alloys Compd. 349 (2003) 232-236.

[8] Y. Kojima, T. Haga, Int. J. Hydrogen Energy. 28 (2003) 989-993.

[9] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder, Int. J. Hydrogen Energy. 25 (2000) 969-975.

[10] S. Özkar, M. Zahmakıran, J. Alloys Compd. 404–406 (2005) 728–731.

[11] P. Krishnan, K.L. Hsueh, S.D. Yim, Appl. Catal. B: Environ. 77 (2007) 206-214.

[12] C.L. Hsueh, C.Y. Chen, J.R. Ku, S.F. Tsai, Y.Y. Hsu, F.H. Tsau, M.S. Jeng, J. Power Sources. 177 (2008) 485-492.

[13] S.U. Jeong, R.K. Kim, E.A. Cho, H.J. Kim, S.W. Nam, I.H. Oh, S.A. Hong, S.H. Kim, J. Power Sources. 144 (2005) 129-134.

[14] J.C. Ingersoll, N. Mani, J.C. Thenmozhiyal, A. Muthaiah, J. Power Sources. 173 (2007) 450-457.

[15] W. Ye, H. Zhang, D. Xu, L. Ma, B. Yi, J. Power Sources. 164 (2007) 544-548.

Table 1: Properties of Dowex 50WX8 resin

Type	Gel strong acid cation exchange resin
Active group	$-SO_3H$
Matrix	styrene-divinylbenzene
Ionic form as shipped	H^+
Standard mesh size (wet)	50 ~ 100 mesh
Moist holding capacity	50% ~ 56%
Total exchange capacity, mEq./mL wet resin	1.7

Table 2: Compositions and Plating Conditions of Electroless Ni Bath and Electroless Ru Bath

	Electroless Ni Bath	Electroless Ru Bath
$NiCl_2 \cdot 6H_2O$	2.62 g/dL	--
$RuCl_3 \cdot xH_2O$	--	2.62 g/dL
$Na_3C_6H_5O_7 \cdot 2H_2O$	4 g/dL	
Maleic acid	0.8 g/dL	
N_2H_4	2.5 ml/dL	
pH	9.5	
Temperature	80°C	
Reaction time	60 min	

Table 3: Surface weight and atomic percentage of the elements present in polymer template (Dowex 50WX8 resin) and catalyst (Ni-Ru/50WX8) by EDS

Elements	Dowex 50WX8 resin		Ni-Ru/50WX8	
	wt %	at %	wt %	at %
C	56.2	67.3	19.3	44.7
O	28.9	26.0	16.7	29.0
S	14.9	6.7	9.2	7.9
Ni	-	-	17.0	8.0
Ru	-	-	37.8	10.4

236 **Figure 1:** EDS spectra of (a) Dowex 50WX8 resin and (b) Ni-Ru/50WX8.

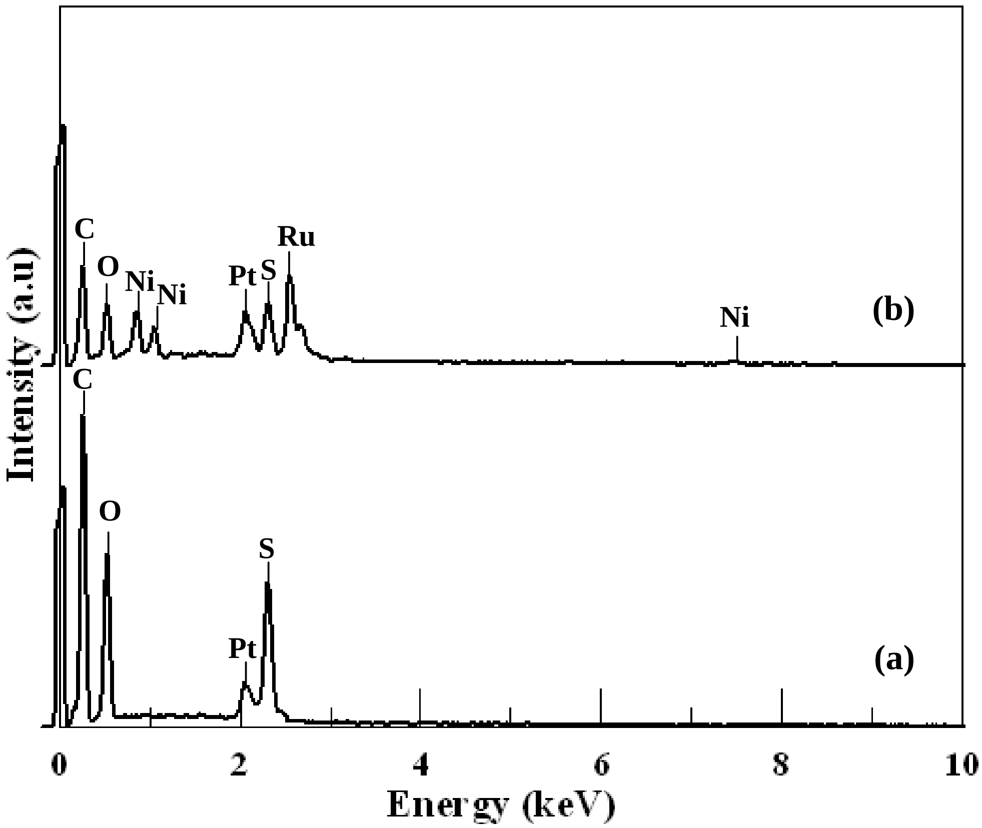
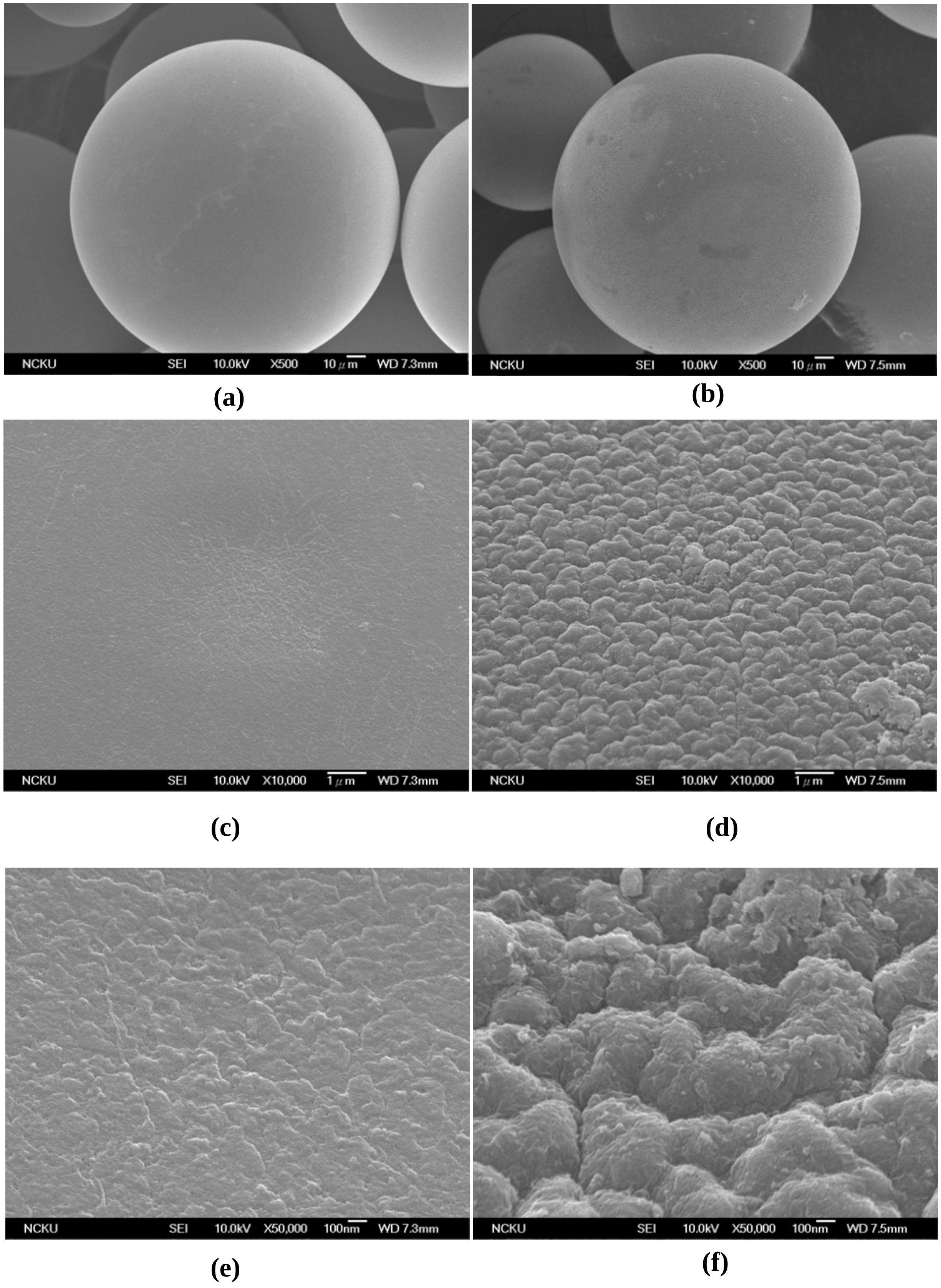


Figure 2: Scanning electron micrographs of (1) Dowex 50WX8: (a) 500×; (c) 10,000×; (e) 50,000×; (2) Ni-Ru/50WX8: (b) 500×; (d) 10000×; (f) 50000×.



(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 3: Volume of hydrogen generated as a function of time in 5 wt% $NaBH_4$ solution containing 200mg Ni-Ru/50WX8 catalyst and different NaOH concentrations at 25 °C.