ELSEVIER

Journal of Alloys and Compounds 379 (2004) 222–227

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Study on degradation of filamentary Ni catalyst on hydrolysis of sodium borohydride

Jin-Ho Kim[a,*], Ki-Tae Kim[a], Yong-Mook Kang[a], Hyun-Seok Kim[a],
Min-Sang Song[a], Yong-Ju Lee[a], Paul S. Lee[b], Jai-Young Lee[a]

[a] *Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology,*
373-1 Gusong-Dong, Yusong-Gu, Daejeon, South Korea
[b] *KLA Tencor, San Jose, CA, USA*

Received 22 December 2003; received in revised form 3 February 2004; accepted 3 February 2004

Abstract

An investigation of durability characteristics of a pasted filamentary Ni catalyst was performed and extensive approaches for elucidating the degradation mechanism of the catalyst were undertaken. The H_2 generation rate of pasted filamentary Ni catalyst gradually decreases with cycling and 76% of the initial H_2 generation rate remains at 200 cycles. After 200 cycles, SEM images show an agglomeration of catalyst particles and a film on the pasted catalyst. An agglomeration of catalyst results in a reduction of specific surface area, as indicated by BET analysis, and a film on the pasted catalyst was formed by an accumulation of potassium originating from alkaline solution, and sodium and boron, which consists of $Na_2B_4O_7{\cdot}10H_2O$, a potassium borate compound (KB_xO_y) and boron oxide (B_2O_3), as indicated by XRD and XPS analyses. Consequently, a deterioration of the catalyst upon hydrolysis of sodium borohydride results from agglomeration of the catalyst and the film formed on the catalyst.

Keywords: Sodium borohydride; Hydrogen; Filamentary Ni; Durability; Degradation

1. Introduction

Hydrogen is forecasted to become a major source of energy in the future. Recently, the use of hydrogen is applied to various industries, while it is anticipated that it will be used extensively if present research and development are continued. Hydrogen is produced from various energy sources, and it is stored, transported and used in industries, homes, automobiles, aeroplanes, and factories, and used in electricity generation. However, for man-portable applications a major hurdle is the development of a means to generate and store controlled amounts of pure H_2 directly without restoring to high temperature reformers with significant heat burner. Recently, numerous studies of hydrogen production through a hydrolysis of sodium borohydride ($NaBH_4$) have been performed by various research groups [2–6]. Schlesinger et al. [1] reported that $NaBH_4$ in aqueous alkaline solutions of pH >11 produces hydrogen gas and water-soluble sodium borate, $NaBO_2$, in the presence of a suitable catalyst.

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 + Q\,(217\,\text{kJ}) \qquad (1)$$

Suda et al. [4] and Kojima et al. [6] examined that the effect of fluorinated metal hydrides and Pt metal, respectively, coated on a metal oxide catalyst on the hydrolysis of $NaBH_4$ in alkaline solution. Amendola et al. [2,3] reported that high H_2 generation rates had been achieved from $NaBH_4$ solution with Ru supported on anion exchange resins. Levy et al. [7] and Kaufman and Sen [8] investigated cobalt and nickel borides as catalysts for practical, controlled generation of H_2 from $NaBH_4$. However, while various catalysts with high H_2 generation rates have been developed through many studies of hydrolysis of sodium borohydride, researches on the durability of catalysts have been scarce.

In the previous work [12], we developed a filamentary Ni mixed Co catalyst with superior performance of short initial waiting time and fast hydrolysis of sodium borohydride. In the present study, the durability characteristics and the approaches for elucidating the degradation mech-

---

* Corresponding author.
E-mail address: fighter@cais.kaist.ac.kr (J.-H. Kim).

0925-8388/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.02.009

anism of a catalyst are extensively studied and reported here.

2. Experimental

At the outset, KOH alkaline solution was used as supporting solution for safe storage of $NaBH_4$ (purchased from Aldrich Inc.). The self-hydrolysis rate of $NaBH_4$ solutions depends on the pH and solution temperature. Kreevoy and Jacobson [9] reported that this rate is empirically represented by:

$$\log t_{1/2} = \mathrm{pH} - (0.034\,T - 1.92) \qquad (2)$$

($t_{1/2}$ is the time required for one-half of the $NaBH_4$ solution to decompose (min) and is dependent on the solution pH and temperature (K)). Hence, the presence of selected catalysts increases the production rate of hydrogen, even in an alkaline solution at normal temperature.

Filamentary Ni (INCO Inc., T-210H, 99.9%), which displays good performance with respect to the hydrolysis of sodium borohydride because of its large specific surface area, was used as a catalyst for hydrolysis of sodium borohydride [12]. The catalyst was prepared by a paste method as explained in our earlier work [10]. The 2 wt.% hydroxypropyl methyl cellulose (HPMC) aqueous solution was obtained by dissolving it in distilled water. This solution has the function of controlling the viscosity of the slurry. Styrene–butadiene rubber (SBR) emulsion, which has tolerance to alkaline solution and hydrophilic property, used as a binding material was stirred vigorously in a vessel with a propeller-type stirrer to prepare the catalyst slurry. Using a doctor-blade technique, the slurry was applied over Ni foam to make a catalyst sheet followed by drying and rolling to a very thin pasted catalyst. Fig. 1 shows the schematic diagram of preparation procedure of pasted catalyst in this study. In this work, all measurements for hydrogen generation rate were conducted at 30 °C by a thermostat.

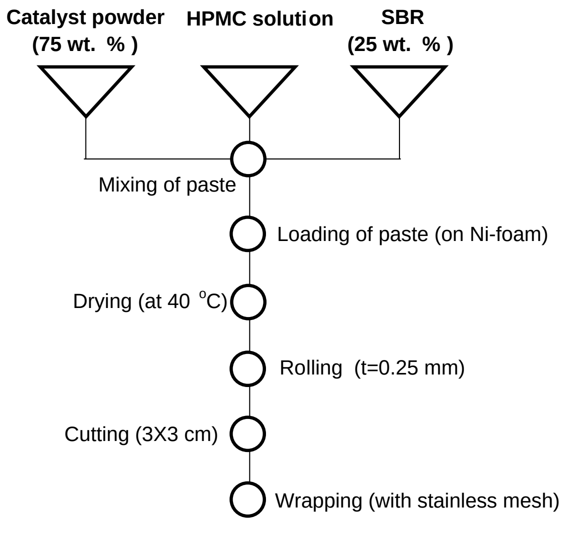


Fig. 1. Schematic of preparation procedure of pasted catalyst.

The structure of the catalyst was studied using an X-ray diffractometer (XRD). Powder X-ray diffraction patterns for these catalysts were obtained on a Rigaku, D/max-IIIC (3 kW) X-ray diffractometer using Cu Kα-source operating at 40 kW and 45 mA. All XRD patterns were recorded at a scan rate of 0.5° $2\theta\,\mathrm{min}^{-1}$, and analyzed by using a MIDI JADE5 program. In order to examine the morphology of the pasted catalyst, scanning electron microscopy (SEM) was employed and the hydrogen gas acquired from hydrolysis of $NaBH_4$ was quantitatively and qualitatively analyzed by gas mass spectroscopy. In order to closely inspect the specific surface area of the pasted catalyst, a volumetric adsorption apparatus (ASAP 2010M) was used through the liquid nitrogen adsorption at 77.35 K by the Brunauer–Emmett–Teller (BET) method. The XPS analysis technique, which was conducted using Mg Kα radiation and an Escalab MKII photoelectron energy spectrum instrument was used to determine the chemical state and content of the constituent elements of the catalyst.

3. Results and discussion

Ni is a promising catalyst with good performance and low cost for the hydrolysis of sodium borohydride [11]. Among various types of Ni powders, filamentary Ni and Raney Ni have good performance in terms of short initial waiting time and efficient hydrolysis of sodium borohydride due to their high specific surface area [12]. In particular, filamentary Ni can be handled very easily and is inexpensive as well as displaying good characteristics for the hydrolysis of $NaBH_4$. In consequence to this, filamentary Ni has been used as a cat-

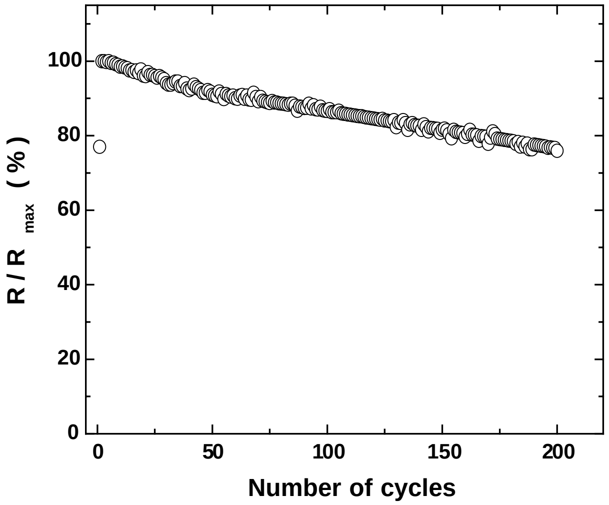


Fig. 2. Cyclic behavior on H_2 generation rate for filamentary Ni catalyst with SBR (20 wt.% of catalyst) over Ni foam immersed in 14 wt.% $NaBH_4$ alkaline solution (pH = 13) at room temperature.

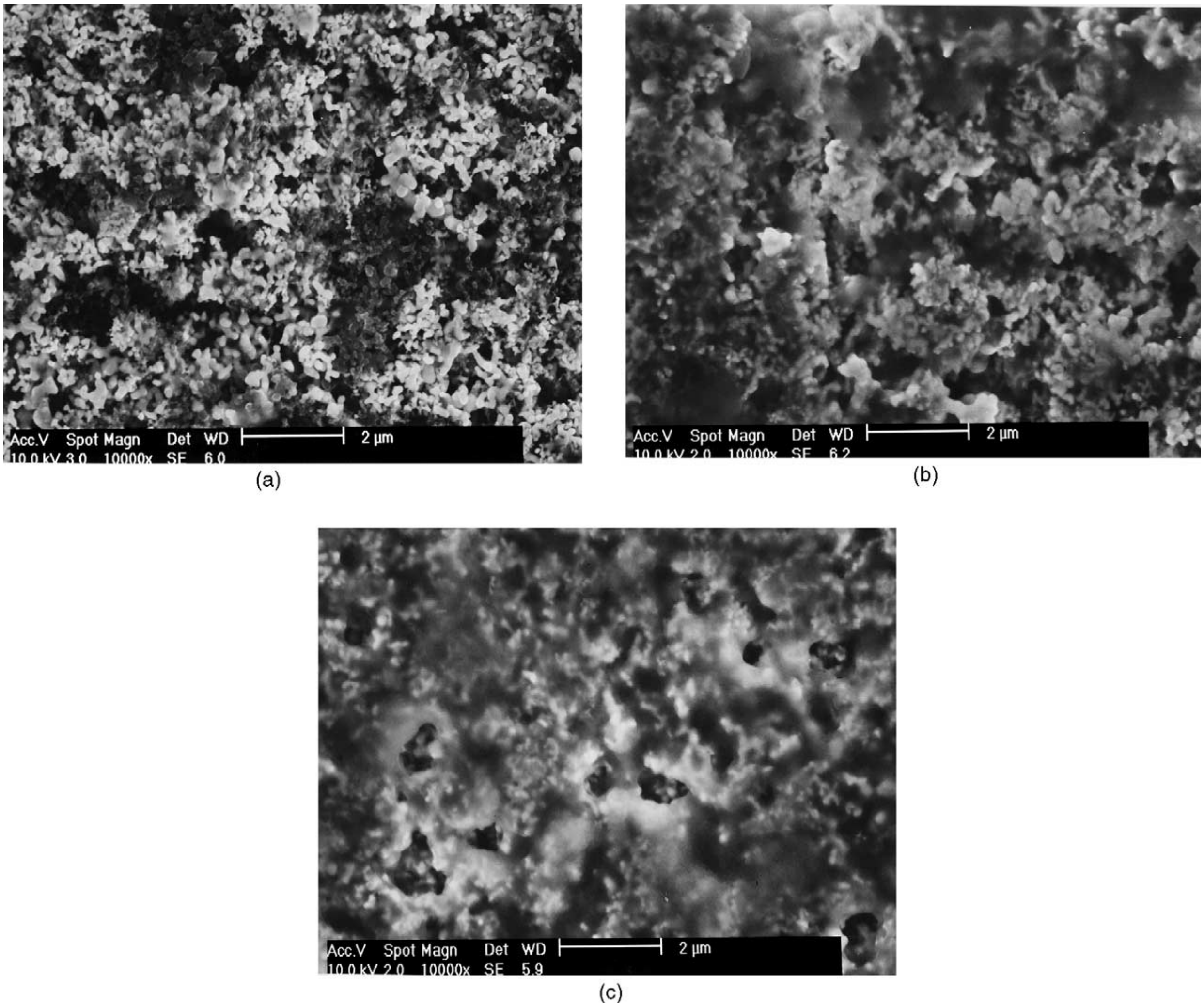
alyst so as to evaluate the cyclic property of the catalyst on the hydrolysis of $NaBH_4$ in an alkaline solution. Fig. 2 plots the cyclic behavior on H_2 generation rate for the pasted filamentary Ni catalyst with SBR (20 wt.% of catalyst loading) over Ni foam in 14 wt.% $NaBH_4$ alkaline solution ($pH = 13$) at room temperature. It is observed that the H_2 generation rate gradually decreases with cycling and only 76% of the initial H_2 generation rate remains at 200 cycles. The degradation mechanism of the catalyst on the hydrolysis of $NaBH_4$ in an alkaline solution is still not clear, and hence attempts have been made to elucidate the degradation mechanism for the pasted filamentary Ni catalyst through SEM, XPS, XRD and BET analyses.

3.1. Formation of film on catalyst

Fig. 3 shows SEM images (10,000×) of the pasted filamentary Ni catalyst before, 100 and 200 cycles, respectively. Peculiarly, with cycling, an unknown film that was not observed prior to cycling was formed and gradually spread over the whole surface of the pasted catalyst. The film formation has not so far been reported, and hence an attempt has been made to test the influence of the film on the degradation of the catalyst.

Fig. 4 plots the cyclic behavior on H_2 generation rate for the pasted filamentary Ni catalyst with and without rinsing with distilled water every cycle. This figure indicates that the pasted filamentary Ni catalyst with rinsing shows better durability than that without rinsing. R/R_{max} value for the pasted catalyst with rinsing and without rinsing was obtained as 93 and 88%, respectively, at the end of 80 cycles. SEM photograph in Fig. 5 shows that even at 80 cycles the film formed on the catalyst as mentioned above was not observed on it due to rinsing. There is a clear improvement on the surface structure of the catalyst in the absence of the film, as compared with the results depicted in Fig. 3. These results imply that the deterioration of the catalyst could be attributed to the film formed on the catalyst. In order to further elucidate the degradation mechanism of the catalyst, the composition of the film was examined.

From EDX analysis, Na and K compositions, which were not detected before cycling, were found to exist together



(a) (b) (c)

Fig. 3. SEM images (10,000×) of the pasted filamentary Ni catalyst: (a) before, (b) after 100, and (c) after 200 cycles.

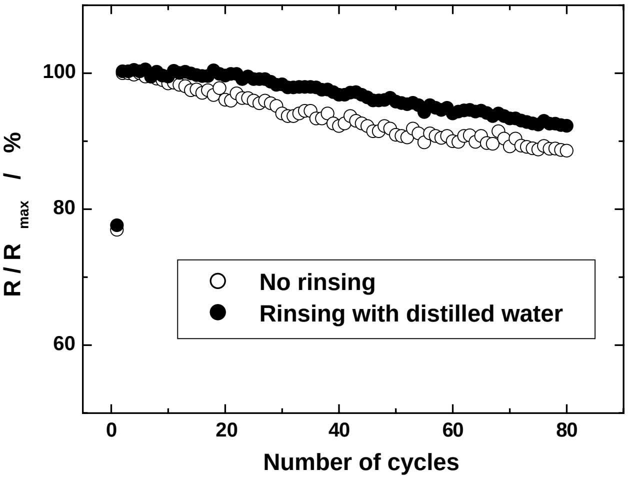


Fig. 4. Cyclic behavior on H_2 generation rate for the pasted filamentary Ni catalyst with and without rinsing with distilled water every cycle.

with Ni on the surface of the catalyst after 200 cycles. Amendola et al. [2] estimated that the precipitation of $NaBO_2$, a by-product on catalyst, would deteriorate a hydrolysis of sodium borohydride, and Kojima et al. [6], using X-ray diffraction, observed $NaBO_2{\cdot}2H_2O$ as a by-product on the hydrolysis of $NaBH_4$ by Pt-TiO_2 catalyst. The film on the catalyst is thus likely to be a compound consisting of Na, K, and other elements. In order to clearly elucidate the unknown film, we have conducted the X-ray diffraction and XPS analysis. From the XRD profile as shown in Fig. 6, Ni is only detected before cycling, while new and small peaks corresponding to $NaB_xO_y{\cdot}nH_2O$ and KB_xO_y are observed after 150 cycles. However, accurate determination of any new phase by XRD analysis is very difficult because XRD peaks of many compounds in hydrated sodium borate or potassium borate group are nearly overlapped with each other. Moreover, XRD analysis is not an effective tool to examine the surface properties. Conversely, XPS analysis is a powerful technique for determining surface states, and hence we have performed XPS analysis to study the chemical changes in the surface of the pasted filamentary Ni catalysts before and after cycling. Fig. 7(a) and (b) display the boron, B, core level spectra of the catalyst before cycling and after 200 cycles, respectively. The peak of elemental boron is assigned to 189.4 eV; this was not observed in Fig. 7(a). The peak around 193 eV indicated in Fig. 7(b) is ascribed to $Na_2B_4O_7{\cdot}10H_2O$ or B_2O_3, which exhibits a chemical shift to high binding energy due to oxidation. Therefore, it is likely that with cycling the hydrated sodium metaborate ($Na_2B_4O_7{\cdot}10H_2O$) stacks upon the pasted catalyst and the

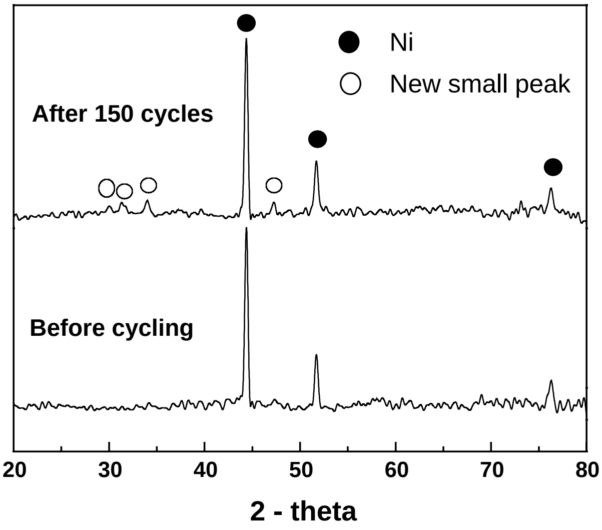


Fig. 6. XRD patterns of filamentary Ni catalyst electrodes before cycling and after 150 cycles.

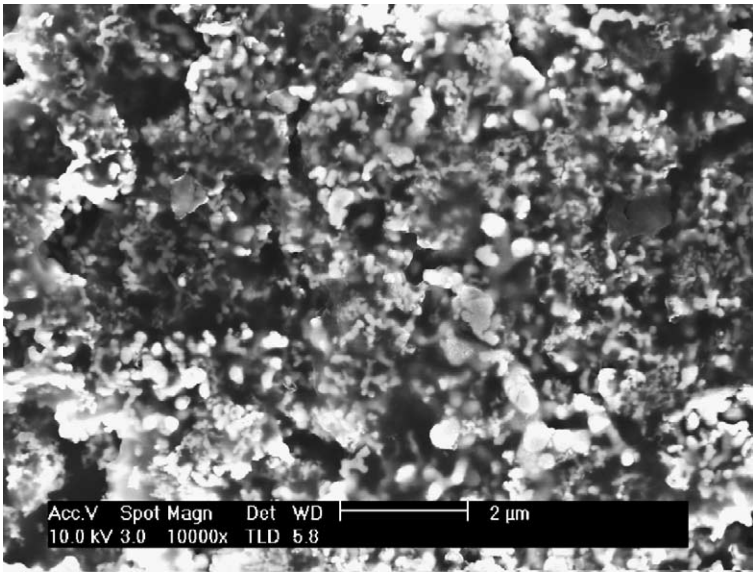


Fig. 5. SEM images (10,000×) of the pasted filamentary Ni catalyst with rinsing after 80 cycles.

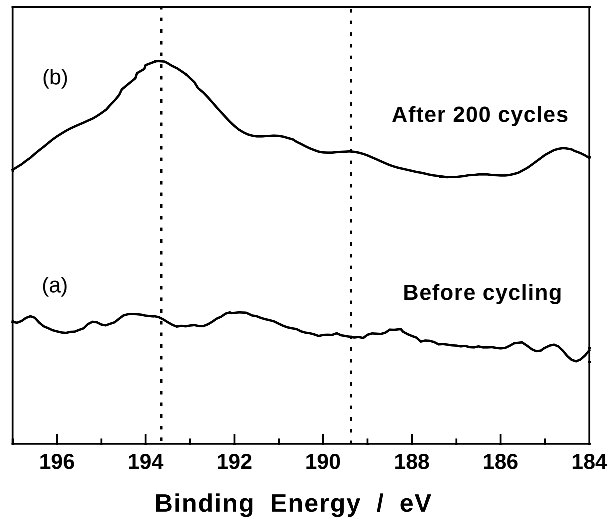


Fig. 7. The boron, B, core level spectra of the catalyst: (a) before cycling and (b) after 200 cycles.

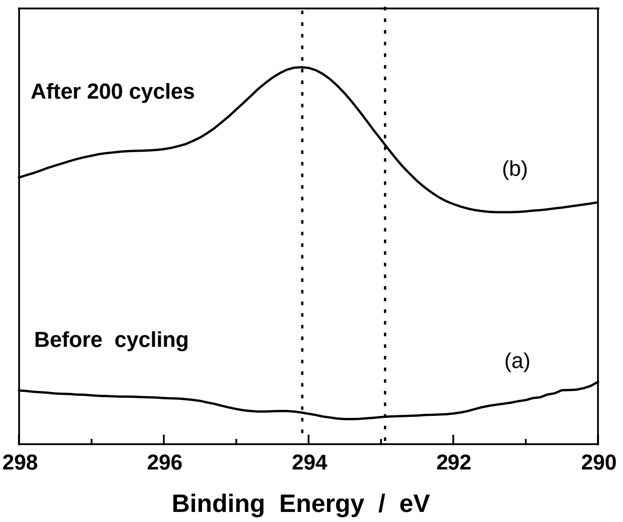


Fig. 9. The potassium, K, core level spectra of the catalyst: (a) before cycling and (b) after 200 cycles.

surface of the catalyst oxidizes, resulting finally in degradation of the catalyst. The sodium, Na, spectra of the pasted filamentary Ni catalyst before cycling and after 200 cycles are displayed in Fig. 8(a) and (b), respectively. The peak of sodium element is assigned to 1072.1 eV; this peak also cannot be observed in Fig. 8(a). Unfortunately, the new peak around 1074 eV in Fig. 8(b) could not be identified what the phase is, however, this strong peak at high binding energy is interpreted as the oxidation of the surface of the pasted filamentary Ni catalyst. Fig. 9(a) and (b) show the potassium, K, spectra of the pasted filamentary Ni catalyst before cycling and after 200 cycles. The peak around 294 eV in Fig. 9(b), shifted to a high binding energy in comparison to elemental potassium, i.e., 292.9 eV, indicates of any kind of potassium borate compound (KB_xO_y), and also implies the oxidation of the surface of the catalyst. From EDX, XRD, and XPS analyses, it is concluded that with cycling, potassium, K, originated in the alkaline solution, and sodium, Na, and boron, B, derived from $NaBH_4$ contact to the surface of catalyst. Therefore, the film which consists of $Na_2B_4O_7\cdot 10H_2O$, unidentified potassium borate (KB_xO_y) and boron oxide (B_2O_3), was formed, resulting in the degradation of the pasted filamentary Ni catalyst.

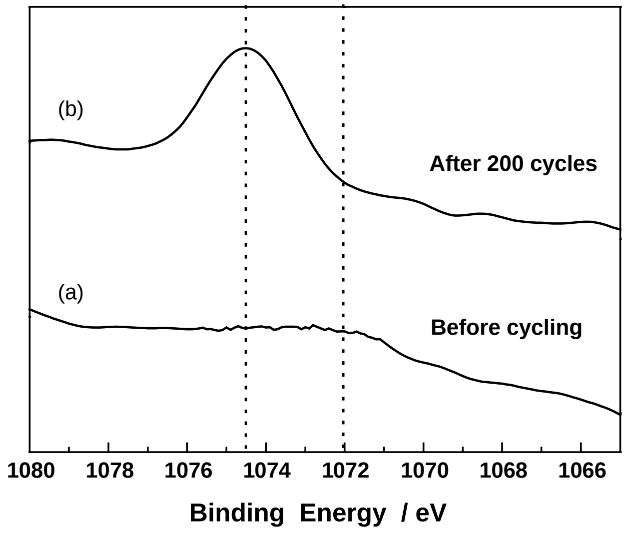


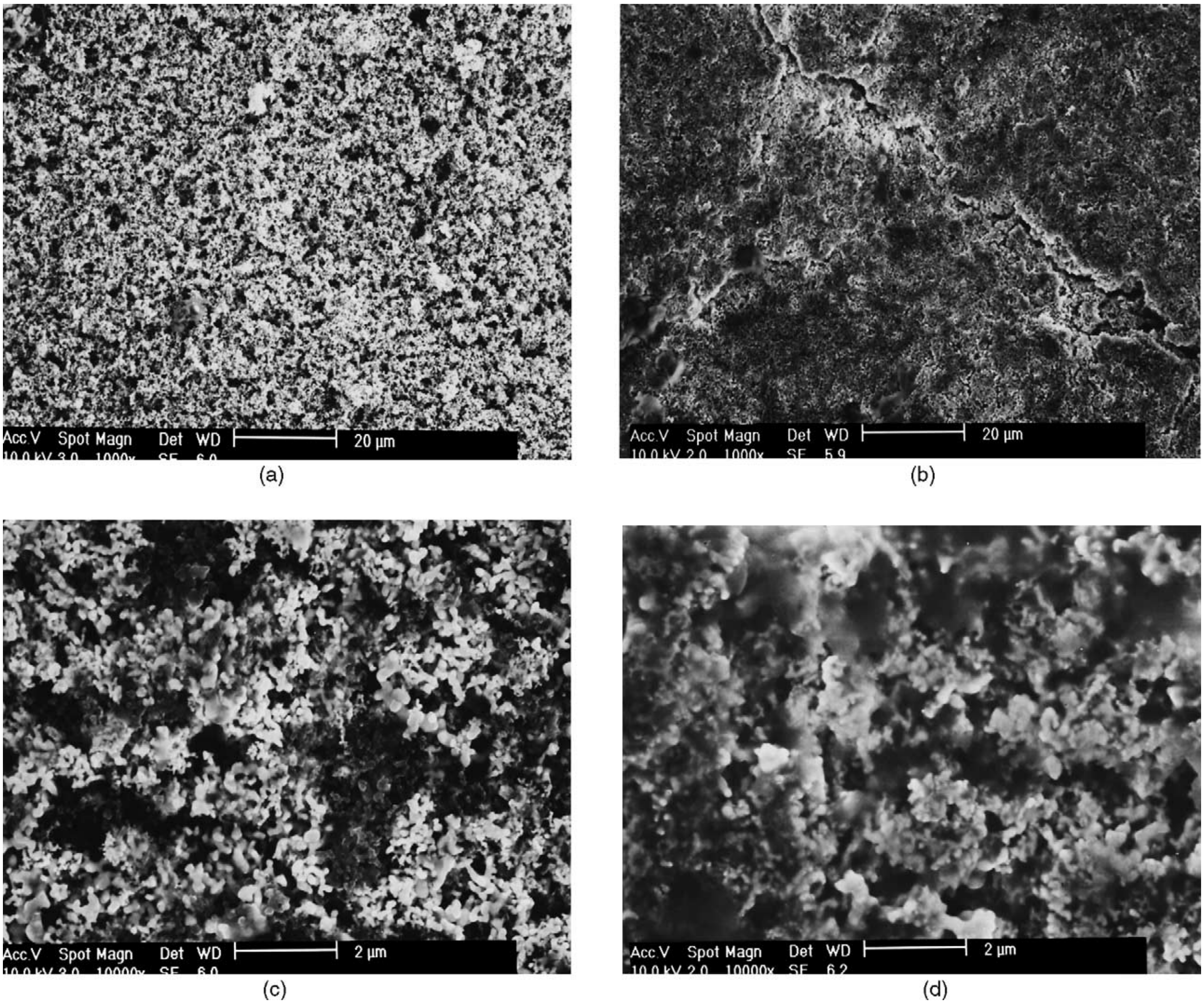
Fig. 8. The sodium, Na, core level spectra of the catalyst: (a) before cycling and (b) after 200 cycles.

3.2. Decrease in specific surface area of catalyst

Fig. 10 shows the low ((a) and (b)) and high ((c) and (d)) magnification of SEM images for the pasted filamentary Ni catalyst before cycling and after 200 cycles. As seen in Fig. 10(a) and (b), an agglomeration of the catalyst is observed with cycling and it is anticipated that this would diminish the specific surface area of the catalyst. Fig. 10(c) and (d), with a higher magnification, show more precise observations of the agglomeration of the catalyst including coarsening of particles with cycling. Also, the BET analysis of the pasted filamentary Ni catalyst before and after 200 cycles, as presented in Table 1, indicates that the specific surface area is decreased by 36.6% after 200 cycles, indicating a reduction of reactive sites on hydrolysis. Therefore, it could be concluded that the second degradation mechanism of the catalyst on the hydrolysis with cycling can be ascribed to the reduction of reactive sites, which results from a decrease of specific surface area induced by the agglomeration of catalysts.

Table 1
BET analysis on specific surface area of filamentary Ni catalyst electrode before cycling and after 200 cycles

	BET surface area (m^2/g)
Before cycling	5.06
After 200 cycles	3.21



(a) (b) (c) (d)

Fig. 10. Low (a) and (b) and high (c) and (d) magnification of SEM images for the pasted filamentary Ni catalyst before cycling and after 200 cycles.

4. Conclusions

H_2 generation rate of filamentary Ni catalyst electrode gently decreases with cycling and 76% of the initial H_2 generation rate remains at 200 cycles. From SEM and BET analyses, the agglomeration of the catalyst was observed and brought about the diminishing of specific surface area of the catalyst electrode with cycling. Therefore, the deterioration of the catalyst with cycling is ascribed to the reduction of reactive sites by a decrease of specific surface area. Also, with cycling, a film not observed prior to cycling, was formed and gradually spreads over the whole surface of the pasted catalyst, eventually covering the reactive sites. From XRD and XPS analyses, it was observed that with cycling, potassium originated from alkaline solution, and sodium and boron accumulated on the surface of pasted catalyst, and finally a film consisting of $Na_2B_4O_7 \cdot 10H_2O$, potassium borate (KB_xO_y) and boron oxide (B_2O_3) was formed. Consequently, a deterioration of the catalyst results from an agglomeration of the catalyst particles and the film formed on the catalyst.

References

[1] H.I. Schlesinger, H.C. Brown, A.B. Finholt, J.R. Gilbreath, H.R. Hockstra, E.K. Hydo, J. Am. Chem. Soc. 75 (1953) 215.
[2] S.C. Amendola, P. Onnerud, M.T. Kelly, P.J. Petillo, S.L. Sharp-Goldman, M. Binder, J. Power Source 85 (2000) 186.
[3] S.C. Amendola, J.M. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, S.L. Sharp-Goldman, M. Binder, Int. J. Hydrogen Energy 25 (2000) 969.
[4] S. Suda, Y.M. Sun, B.H. Liu, Y. Zhou, S. Morimitsu, K. Aral, N. Tskamoto, M. Uchida, Y. Caudra, Z.P. Li, Appl. Phys. A 72 (2001) 209.
[5] I.I. Korovov, N.G. Mozgina, L.N. Blinova, Kinet. Catal. 36 (3) (1995) 380.
[6] Y. Kojima, K.I. Suzuki, K. Fukumoto, M. Sakai, T. Yamamoto, Y. Kawai, H. Hayashi, Int. J. Hydrogen Energy 27 (2002) 1029.
[7] A. Levy, J.B. Brown, C.J. Lyons, Ind. Eng. Chem. 52 (1960) 211.
[8] C.M. Kaufman, B. Sen, J. Chem. Soc. Dalton Trans. (1985) 307.
[9] Kreevoy, M.M. Jacobson, Ventron Alembic, 1979, pp. 2–3.
[10] D.M. Kim, H. Lee, K.J. Jang, J.Y. Lee, J. Electrochem. Soc. 145 (10) (1998) 3387.
[11] H.C. Brown, C.A. Brown, J. Am. Chem. Soc. 84 (1962) 1493.
[12] J.H. Kim, H. Lee, S.C. Han, H.S. Kim, M.S. Song, J.Y. Lee, Int. J. Hydrogen Energy 29 (2004) 263–267.