



Studies on catalytic behavior of Co–Ni–B in hydrogen production by hydrolysis of NaBH₄

R. Fernandes^{a,*}, N. Patel^a, A. Miotello^a, M. Filippi^b

^a Dipartimento di Fisica, Università degli Studi di Trento, I-38100 Povo (Trento), Italy

^b Fondazione Bruno Kessler – Ricerca Scientifica e Tecnologica, I-38100 Povo (Trento), Italy

ARTICLE INFO

Article history:

Received 1 August 2008

Received in revised form 4 September 2008

Accepted 4 September 2008

Available online 20 September 2008

Keywords:

H₂ generation

Hydrolysis

Sodium borohydride

Co–Ni–B catalyst

ABSTRACT

Catalyst powders of Co–B, Ni–B, and Co–Ni–B, with different molar ratios of Co/Ni, were synthesized by chemical reduction of cobalt and nickel salts with sodium borohydride at room temperature. Surface morphology and structural properties of the catalyst powders were studied using scanning electron microscopy (SEM) and X-ray diffraction (XRD) respectively. Surface electronic states and composition of the catalysts were studied by X-ray photoelectron spectroscopy (XPS). The catalytic activity of the powders has been tested by measuring the H₂ generation rate and yield by the hydrolysis of NaBH₄ in basic medium. Co–Ni–B with the Co/(Co + Ni) molar ratio (χ_{Co}) of 0.85 exhibited much superior activity with highest H₂ generation rate as compared to the other powder catalysts. The enhanced activity obtained with Co–Ni–B ($\chi_{\text{Co}} = 0.85$) powder catalyst could be attributed to: large active surface area and electron transfer by alloying large quantity of B to active Co and Ni sites on the surface of the catalyst. The electron enrichment, detected in the XPS spectra on active Co and Ni sites in Co–Ni–B, higher than that of Co–B and Ni–B seems to be able to facilitate the catalysis reaction by providing the negative charge electron required by the reaction. Synergetic effect of the Co and Ni atoms in Co–Ni–B catalyst is able to lower the activation energy up to 34 kJ mol⁻¹ as compared to 45 kJ mol⁻¹ obtained with Co–B powder. Structural modification, caused by the heat-treatment at 773 K for 2 h in Ar atmosphere, was not able to change the activity of the Co–Ni–B powder.

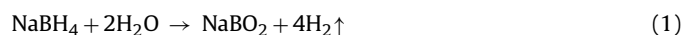
© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a clean and efficient alternative power source for transportation and personal electronics applications, where low system weight and portability are important. Pure hydrogen is used as the fuel in PEMFC [1] but on industrial level, H₂ is mostly produced by steam reforming of natural gas and so the final product contains carbon contamination (CO₂ and CO). The presence of carbon monoxide (even at ppm level) in the hydrogen gas reduces the performance of PEMFC because of catalyst poisoning [2].

Chemical hydrides are very attractive materials for pure hydrogen supply to the fuel cells at room temperature [3]. Among them, aqueous sodium borohydride (NaBH₄) seems to be an ideal hydrogen source because it is stable, non-flammable and non-toxic in nature with hydrogen storing capability of 10.8 wt.% [4]. The reaction product (borax), obtained after removal of hydrogen from NaBH₄, is environmentally clean and can be recycled to generate

the reactant [5]. Hydrogen is generated from NaBH₄ by following hydrolysis reaction, with the important advantage of producing half of the hydrogen from the water solvent [6]:



The efficiency of hydrogen production can be significantly enhanced by use of catalyst during the reaction. Many organic and inorganic acids are able to effectively enhance the hydrolysis reaction rate; however the reaction usually becomes uncontrollable [7]. On other hand, solid state catalysts such as precious (generally functionalized with support) or transition metals and their salts are found to be very efficient in accelerating the hydrolysis reaction in a controllable manner.

Catalysts like Ru supported on anion-exchange resin [8], fluorinated Mg based alloy [9], Pt [10] and Pd supported on carbon [11], PtRu supported on metal oxide [12], raney Ni and Co, and even nickel and cobalt borides [13–15] are generally used to accelerate the hydrolysis reaction of the NaBH₄. Co and Ni borides are mostly considered as good candidates for catalyzed hydrolysis reaction of NaBH₄ owing to their good catalytic activity and low cost. These catalyst materials can be effortlessly synthesized by the simple procedure of chemical reduction method by which transition metal

* Corresponding author.

E-mail address: fernandes@science.unitn.it (R. Fernandes).

ions are brought to the metallic state by reducing agent [14]. In our previous work, Co–B catalysts developed in form of films showed a performance similar to the noble metals [15,16]. It was also found that these non-noble metals (Co and Ni) demonstrate the better activity only when used in boride form because boron is able to protect the active metal sites (Co or Ni) from oxidation by electron transfer [17]. Thus, it is important to understand the role of boron to achieve the best configuration/composition for the catalyst. The recent work of Li et al. [18] demonstrates that the mixed boride in form of Co–Ni–B is able to better work for the hydrogenation of nitriles just because of the boron enrichment on the surface. Recently, Co–Ni–B catalyst was also used for the hydrolysis of NaBH₄ [19] but the authors did not studied the role of the atomic elements concentration in the catalyst because they only used a single Co/(Co + Ni) molar ratio (χ_{Co}) equal to 0.50.

In our present work, we examined several Co/Ni atomic ratios in Co–Ni–B catalyst in order to establish the optimum condition to have the best efficiency in the catalytic reaction. We discovered indeed that, Co/Ni ratio is an important parameter to determine the efficiency of the catalyst, a result non-previously reported. In addition, we have also compared Co–Ni–B catalyst with Co–B and Ni–B in order to understand the role of each atomic element in the catalytic activity, by also specifically looking at the XPS results on binding electron energies. The favourable activation energy value obtained with Co–Ni–B, as compared to Co–B, suggests that electronic synergetic effects operate with Co and Ni atoms in Co–Ni–B which help to enhance the catalytic activity. Possibly, transient electronic states are favoured with Co and Ni atoms in the Co–Ni–B powder at appropriate atomic composition. This new research activity is important to contribute to possible application to on-board reactor.

2. Experimental

2.1. Catalyst preparation

Co–Ni–B catalysts were prepared by adding NaBH₄ as reducing agent into the aqueous mixture solution of cobalt chloride (CoCl₂) and nickel chloride (NiCl₂) under vigorous stirring at room temperature. Excess amount of borohydride was used in order to completely reduce Co and Ni cations to metals. The resulting black powder, separated from solution during reaction course, was filtered, extensively washed with distilled water and ethanol (99.9%) in order to remove Cl⁻ and Na⁺ ions, and then dried in continuous nitrogen flow at around 323 K.

The Co/(Co + Ni) molar ratio (χ_{Co}) in the Co–Ni–B samples was adjusted by varying the concentration of Co and Ni salts in the starting solution. Ni–B ($\chi_{\text{Co}} = 0$) and Co–B ($\chi_{\text{Co}} = 1$) were also prepared in a similar manner when only NiCl₂ or CoCl₂ was used in the solution respectively. One set of Co–Ni–B and Co–B powder was annealed at 773 K for 2 h in Ar atmosphere to study the effect of the lattice structural variation on the catalytic activity.

2.2. Catalyst characterization

The surface morphologies of all catalyst powders were studied by scanning electron microscope (SEM-FEG, JSM 7001F, JEOL) equipped with energy-dispersive spectroscopy analysis (EDS, INCA PentaFET-x3) to verify the composition of the samples. Structural characterization of the catalyst powders was determined by conventional X-ray diffraction (XRD) using the Cu K α radiation ($\lambda = 1.5414 \text{ \AA}$) in Bragg–Brentano (θ – 2θ) configuration.

The studies on surface electronic states and composition of the catalysts were carried out by X-ray photoelectron spectroscopy (XPS). XPS spectra were acquired within a SCIENTIA ESCA200 instru-

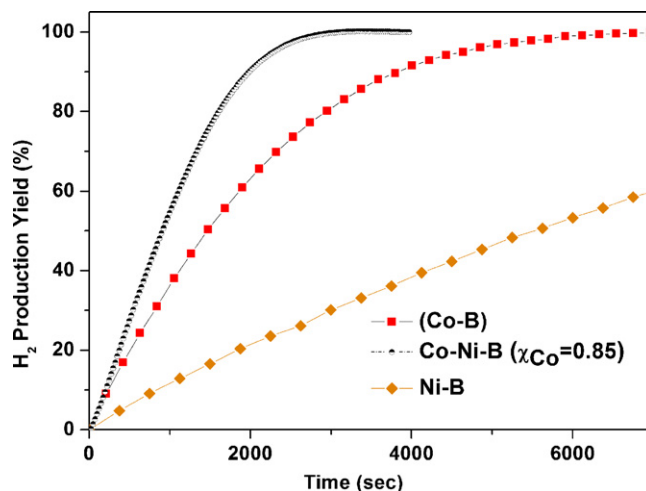


Fig. 1. Hydrogen generation yield as a function of reaction time obtained by hydrolysis of alkaline NaBH₄ (0.025 M) with Co–B, Ni–B, and Co–Ni–B ($\chi_{\text{Co}} = 0.85$) catalyst powder.

ment equipped with a monochromatic Al K α (1486.6 eV) X-ray source and a hemispherical analyzer. No electrical charge compensation was required to perform the analysis.

2.3. Activity measurement

For catalytic activity measurements, an alkaline-stabilized solution of sodium borohydride (pH 13, $0.025 \pm 0.001 \text{ M}$) (Rohm and Haas), was prepared by addition of NaOH (0.025 M). The titre of reagent was independently measured through iodometric method [20]. The hydrogen generation rate was measured through a gas volumetric method in an appropriate reaction chamber with thermostatic bath, wherein the temperature was kept constant within accuracy $\pm 0.1 \text{ K}$. The chamber was equipped with pressure sensor, stirrer system, catalyst insertion device and also coupled with an electronic precision balance to accurately measure the weight of water volumes displaced by the hydrogen volumes produced during the reaction course. A detailed description of the measurement apparatus is given in Ref. [21]. In all the runs, the catalyst was placed on the appropriate device inside the reaction chamber and the system was sealed. In order to make comparison we plot the time dependences versus stoichiometric hydrogen production yield (%) instead of hydrogen volume (ml). Catalyst powder was added to 200 ml of the above solution under continuous stirring.

3. Results and discussion

Fig. 1 presents the hydrogen generation yield as function of time obtained by the hydrolysis of alkaline NaBH₄ (0.025 M) solution using Co–B, Ni–B, and Co–Ni–B ($\chi_{\text{Co}} = 0.85$) catalyst powder at 298 K. The expected total amount of H₂ has been measured, no matter of the type of catalyst used. The generation rate initially increases to a maximum value and then decreases with time as the NaBH₄ concentration decreases in the solution: this suggests the non-zero order of the reaction kinetics. Co–Ni–B ($\chi_{\text{Co}} = 0.85$) catalyst shows much better catalytic activity as compared to the same amount ($\approx 15 \text{ mg}$) of Co–B and Ni–B powder. Fitting method as mentioned in our previous work [15] has been utilized to obtain maximum hydrogen generation rates (R_{max}) which are summarized in Table 1. Co–Ni–B ($\chi_{\text{Co}} = 0.85$) shows the highest R_{max} which is nearly 1.7 and 11.5 times higher than the Co–B and Ni–B powder, respectively.

Table 1

Maximum hydrogen generation rate obtained with Co–B, Co–Ni–B ($\chi_{\text{Co}} = 0.50, 0.65, 0.75, 0.85,$ and 0.90) and Ni–B powders by hydrolysis of alkaline NaBH_4 (0.025 M) solution.

Catalyst powder	Co/(Co + Ni) molar ratio (χ_{Co})	Maximum hydrogen generation rate (ml/(min g) catalyst)
Ni–B	0	~100
Co–Ni–B	0.50	~491
Co–Ni–B	0.65	~644
Co–Ni–B	0.75	~832
Co–Ni–B	0.85	~1175
Co–Ni–B	0.90	~779
Co–B	1	~681

In Fig. 2 we present SEM images of Co–B, Co–Ni–B ($\chi_{\text{Co}} = 0.85$), and Ni–B powders. Both Co–B and Ni–B are present in form of well-dispersed spherical particles with the average size of about 30 and 18 nm, respectively. In the case of Co–Ni–B catalyst the particles sizes seem to be smaller as compared to the other powders and they are difficult to measure because they are embedded in cotton-like filamentary matrix of nanometer size. This kind of morphology might be helpful to enhance the active surface area of the Co–Ni–B catalyst. XRD pattern (figure not shown) of Co–B, Co–Ni–B ($\chi_{\text{Co}} = 0.85$), and Ni–B powders showed a single broad peak at around $2\theta = 45^\circ$ thus indicating the amorphous nature of the catalyst powders. The SEM and XRD results obtained in the present case are consistent with those reported in the literatures [18,22].

To try to understand the enhanced activity of Co–Ni–B ($\chi_{\text{Co}} = 0.85$), it is necessary to study the surface electronic interaction between the atoms in the compound. Thus, XPS spectra of Co–B, Co–Ni–B ($\chi_{\text{Co}} = 0.85$), and Ni–B catalyst powders were acquired and reported in Fig. 3. In all the catalyst powders, two peaks appear in $\text{Co}_{2p_{3/2}}$ and $\text{Ni}_{2p_{3/2}}$ levels with the binding energies of 778.4 and 781.9 eV for Co, and 852.8 and 856.3 eV for Ni indicating that metals exist in both the elemental and oxidized states respectively. The peaks due to oxidized Co and Ni are mainly related to $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ which would have been formed during the catalyst preparation reaction between NaBH_4 and metal salts [23,24]. Two XPS peaks with binding energy (BE) of 188.1 and 192.5 eV are also observed for the B_{1s} level, which are assigned to elemental and oxidized boron, respectively [23]. If one compares the BE of pure boron (187.1 eV) [25] with that of the elemental boron in all the catalyst powders there is positive shift of 1 eV. This shift indicates an electron transfer from alloying B to vacant d-orbital of metallic Ni and/or Co which makes boron electron deficient while Ni and/or Co metals are enriched with the electron in all the catalyst powders. Electron-enriched metal active sites repel the adsorption of oxygen atoms while they are strongly adsorbed by the electron-deficient B. In other words, alloying B effectively protects metals from oxidation [26,27]. The BE of metallic Co in Co–Ni–B is 0.2 eV lower than that in the Co–B, whereas BE of metallic Ni in Co–Ni–B is 0.1 eV lower than that in Ni–B. This proves that in Co–Ni–B catalyst,

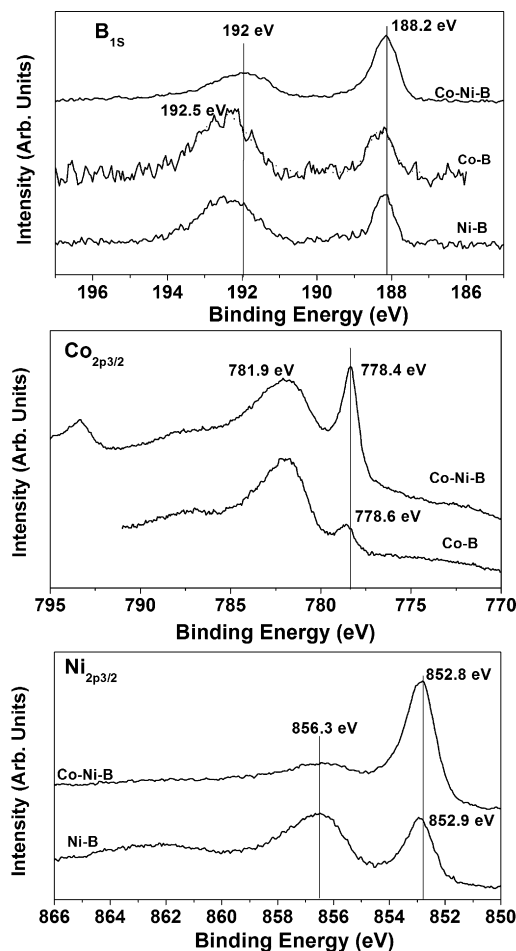


Fig. 3. XPS spectra of B_{1s} , $\text{Co}_{2p_{3/2}}$ and $\text{Ni}_{2p_{3/2}}$ level for Co–B, Ni–B, and Co–Ni–B ($\chi_{\text{Co}} = 0.85$) catalyst powder.

Table 2

Surface atomic composition of catalyst powders obtained by the XPS spectra.

Catalyst powders	Co (at.%)	Ni (at.%)	B (at.%)
Co–B	64	–	36
Co–Ni–B ($\chi_{\text{Co}} = 0.85$)	50	9	41
Ni–B	–	64	39

Co and Ni metals may exchange electrons more easily than the Co–B and Ni–B catalyst: this could be connected to the B-enrichment in Co–Ni–B catalyst as seen by the compositional analysis of XPS spectra (Table 2) and also reported by Li et al. [18] who also performed theoretical calculations using DFT method to show that the increase of the B content on surface would contribute more

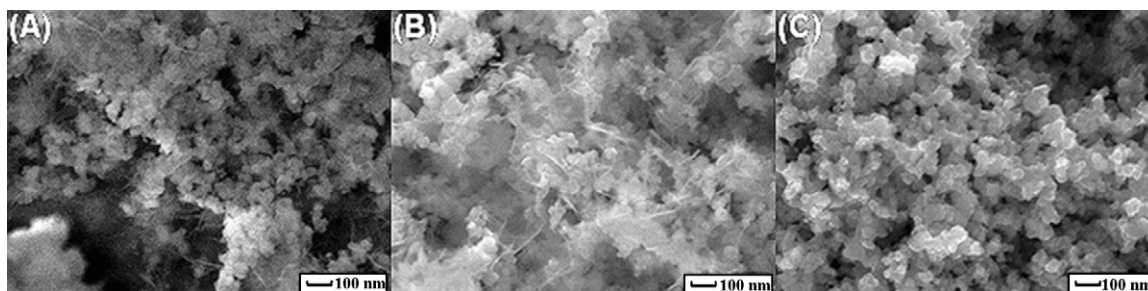


Fig. 2. SEM micrographs of (A) Ni–B, (B) Co–Ni–B ($\chi_{\text{Co}} = 0.85$) and (C) Co–B catalyst powder.

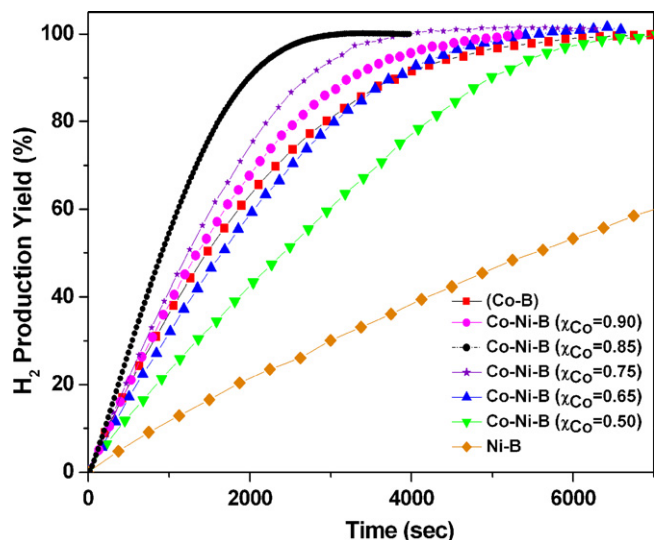


Fig. 4. Hydrogen generation yield as a function of reaction time obtained by hydrolysis of alkaline NaBH_4 (0.025 M) with Ni-B, Co-Ni-B ($\chi_{Co} = 0.50, 0.65, 0.75, 0.85$, and 0.90) and Co-B catalyst powder.

electrons to metallic Ni or Co in their corresponding amorphous alloys.

The H_2 production from the metal-catalyzed hydrolysis of NaBH_4 is proposed to take place by following three kinetics steps [11]. In the first step, BH_4^- ions are chemisorbed on the metal (Ni and/or Co) atoms while in the second step the hydride ion H^- is transferred from BH_4^- ion to an unoccupied adjacent (Ni and/or Co) metal atom. In the last step, this hydrogen atom acquires a negative charge in form of electron from the metal and leaves the site in hydridic form (H^-) which reacts with the water molecule to produce H_2 and OH^- ion. OH^- reacts with boron in BH_3 to produce the $\text{BH}_3(\text{OH})^-$ ion. The cycle of hydrogen absorption on the metal sites continues till $\text{BH}_3(\text{OH})^-$ forms $\text{B}(\text{OH})_4^-$. Molecular hydrogen is released during the full cycle. Looking at the mechanism mentioned above, electron enriched metal active sites will be able to facilitate the catalysis reaction by providing the negative charge electron required by the hydrogen atom in the last step. These electrons are provided by the alloying boron to the active metal sites, as discussed when reporting the XPS results. Thus, the higher concentration of boron in Co-Ni-B catalyst, as compared to Co-B and Ni-B, plays a significant role in enhancing the catalytic activity.

Co and Ni molar ratio was varied from $\chi_{Co} = 0.5$ to 0.9 in the Co-Ni-B powder catalyst in order to study the effect of active metal concentration on catalytic activity. The Co and Ni molar ratio was evaluated by EDS and XPS. Fig. 4 presents the hydrogen generation yield as function of time measured by hydrolysis of alkaline NaBH_4 (0.025 M) solution using Co-Ni-B catalyst powder with different molar ratio of Ni and Co. The corresponding maximum H_2 generation rate (R_{max}) is report in Table 1. R_{max} obtained by pure Ni-B catalyst is always lower than that measured by other powders containing Co. By increasing the Co content relative to Ni in the Co-Ni-B powder, the rate increases and reaches the highest R_{max} of about ~ 1175 ml/min/g for molar ratio of $\chi_{Co} = 0.85$ which is even superior than pure Co-B powder. With further increase of the molar ratio χ_{Co} to 0.9, the activity of the powder decreases. The catalytic activity of the powders decrease in following order: Co-Ni-B ($\chi_{Co} = 0.85$) > Co-Ni-B ($\chi_{Co} = 0.75$) > Co-Ni-B ($\chi_{Co} = 0.90$) > Co-B ($\chi_{Co} = 1$) > Co-Ni-B ($\chi_{Co} = 0.65$) > Co-Ni-B ($\chi_{Co} = 0.50$) > Ni-B ($\chi_{Co} = 0$). The measurements were repeated at least three times to verify the results obtained in the present case. As observed in the previous results, the Co-B shows much higher catalytic activity

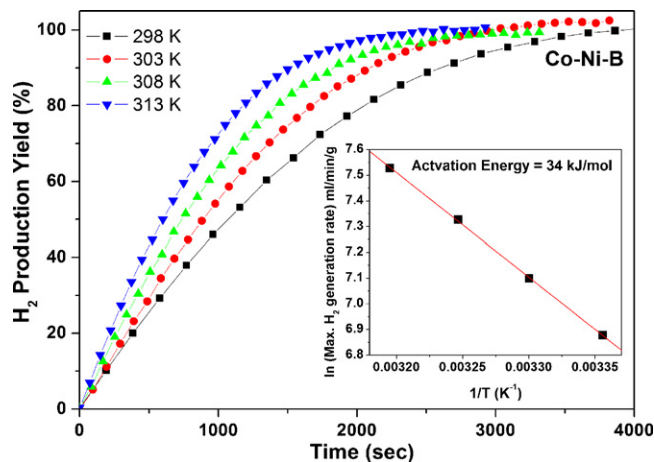


Fig. 5. Hydrogen generation yield as a function of reaction time with Co-Ni-B ($\chi_{Co} = 0.85$) catalyst measured at four different temperatures by hydrolysis of alkaline NaBH_4 (0.025 M) solution. Inset shows the Arrhenius plot of the H_2 generation rates with Co-Ni-B ($\chi_{Co} = 0.85$) powder.

as compared to Ni-B thus indicating that Co metal is more active site than Ni for catalytic hydrolysis reaction. The increment in the activity by increasing the amount in Co is due to the fact that less active Ni sites are replaced by more active Co sites. However, the effect of B enrichment on the surface of the Co-Ni-B ($\chi_{Co} = 0.90, 0.85$ and 0.75) causes the superior activity than Co-B as discussed previously.

In another set of experiments, the hydrogen generation from catalytic hydrolysis of alkaline NaBH_4 (0.025 M) solution was measured at different solution temperature ranging from 298 to 313 K by using Co-Ni-B ($\chi_{Co} = 0.85$) (Fig. 5) and Co-B (Fig. 6) catalyst powders. As expected, H_2 generation rate increases with the temperature. The Arrhenius plot (inset of Fig. 5 and Fig. 6) of the hydrogen production rate gives activation energies of about 34 ± 1 and 45 ± 2 kJ mol^{-1} , within experimental errors, for Co-Ni-B ($\chi_{Co} = 0.85$) and Co-B powder catalyst, respectively. This value for Co-Ni-B powder is lower than that found by Amendola et al. [8] using Ru catalyst (47 kJ mol^{-1}), while Kaufman and Sen [28] obtained 75 kJ mol^{-1} for Ni, and 63 kJ mol^{-1} for Raney nickel. The activation energy for the Co-B catalyst mea-

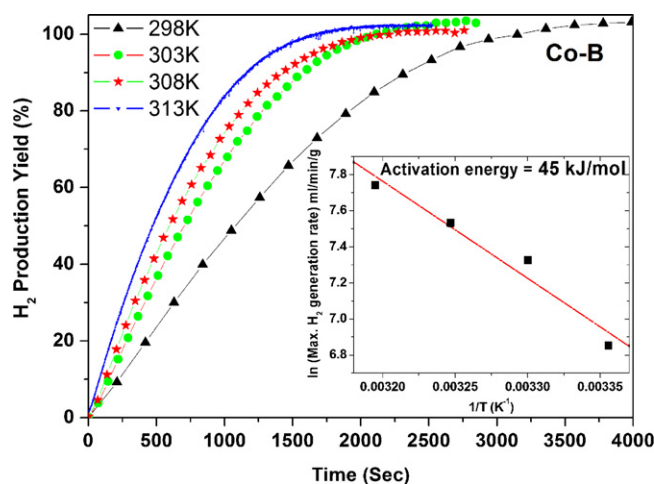


Fig. 6. Hydrogen generation yield as a function of reaction time with Co-B catalyst measured at four different temperatures by hydrolysis of alkaline NaBH_4 (0.025 M) solution. Inset shows the Arrhenius plot of the H_2 generation rates with Co-B powder.

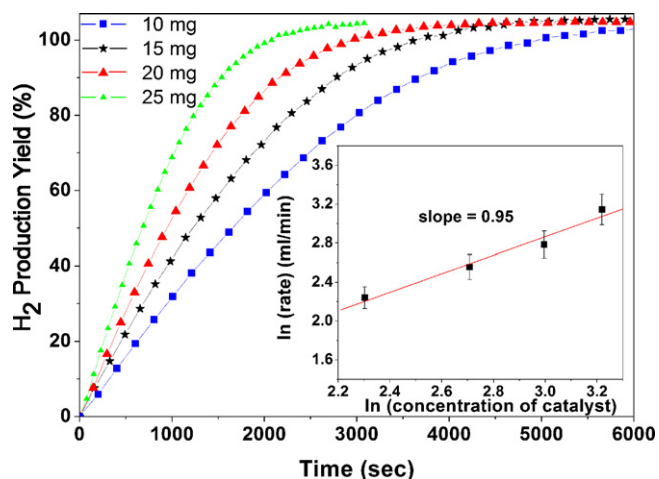


Fig. 7. Hydrogen generation yield as a function of reaction time with Co-Ni-B ($\chi_{\text{Co}}=0.85$) catalyst of four different concentrations by hydrolysis of alkaline NaBH_4 (0.025 M) solution. Inset shows the plot of $\ln(\text{H}_2$ generation rate) vs. $\ln(\text{concentration of catalyst})$.

sured in the present case is same as that obtained by Lee et al. [6] with structured Co-B catalyst powder (45 kJ mol^{-1}). The activation energy of about 62 kJ mol^{-1} is reported by Ingersoll et al. [19] by using Co-Ni-B powder catalyst with similar atomic concentration of Co and Ni. Our results are for $\chi_{\text{Co}}=0.85$. The favourable activation energy value obtained with Co-Ni-B, as compared to Co-B, suggests that electronic synergetic effects operate with Co and Ni atoms in Co-Ni-B which help to enhance the catalytic activity. Possibly, transient electronic states are favoured with Co and Ni atoms in the Co-Ni-B powder at appropriate atomic composition.

To identify the reaction order in connection to the catalyst concentration, the H_2 generation yield was measured by hydrolysis of alkaline NaBH_4 (0.025 M) solution using four different amounts of Co-Ni-B ($\chi_{\text{Co}}=0.85$) catalyst, i.e., 10, 15, 20, 25 mg (Fig. 7) at 298 K. The figure clearly indicates that the hydrolysis of NaBH_4 depends on the catalyst concentration because when the amount of catalyst increases, then the reaction takes much less time to reach the maximum expected H_2 generation yield. The hydrogen generation rate (R) seems to be proportional to the catalyst concentration when the concentrations of all the other reactants are kept constant:

$$R \propto [\text{concentration of catalyst}]^x \quad (2)$$

By plotting $\ln(R)$ vs. $\ln(\text{concentration of catalyst})$ one obtains the straight line of the inset of Fig. 7 and the slope provides the value of the reaction order (x) with respect to the concentration of catalyst.

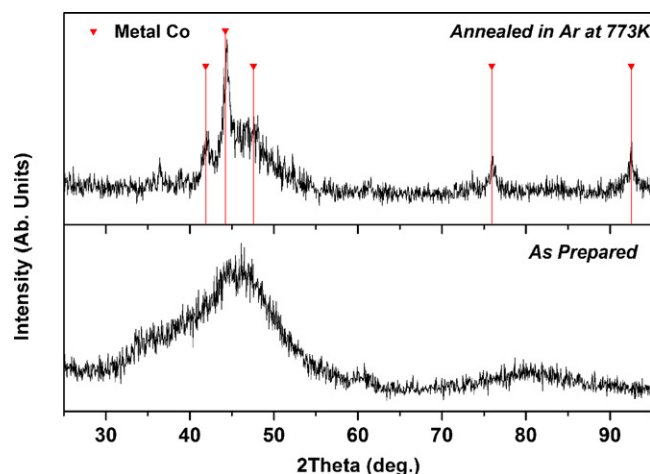


Fig. 8. XRD pattern of Co-Ni-B ($\chi_{\text{Co}}=0.85$) catalyst powder untreated and treated in Ar gas atmosphere at 773 K for 2 h.

The value of the slope is 0.95 thus indicating that the hydrolysis of NaBH_4 is first order reaction with respect to the concentration of Co-Ni-B ($\chi_{\text{Co}}=0.85$) powder catalyst.

To study the effect of structural modification on catalytic activity, Co-Ni-B ($\chi_{\text{Co}}=0.85$) and Co-B were heat-treated in Ar atmosphere at 773 K for 2 h. XRD pattern (Fig. 8) of the annealed Co-Ni-B ($\chi_{\text{Co}}=0.85$) powder show that annealing causes structural modification in the powder leading to the formation of crystalline Co metal phase with the crystal size of around 15 nm. Morphological studies performed by SEM also show analogous results for annealed Co-Ni-B powder catalyst. The SEM images (Fig. 9) clearly demonstrate the transformation from the well-dispersed spherical particle morphology of the fresh powders (Fig. 9A) to porous crystallite morphology after annealing at 773 K (Fig. 9B). The hydrogen generation yield, as function of time, obtained by hydrolysis of alkaline NaBH_4 (0.025 M) solution using annealed Co-Ni-B ($\chi_{\text{Co}}=0.85$) at 293 K, is reported in Fig. 10. However, the structural changes did not bring any differences in the catalytic activity for the annealed Co-Ni-B ($\chi_{\text{Co}}=0.85$) powder when compared with untreated powder. Co-B powder annealed at 773 K in similar condition, shows analogous structural modification similar to that of Co-Ni-B. However, there is now a decrease in the hydrogen generation rate as compared to the untreated powder (Fig. 11). Lee et al. [6] and Wu et al. [29] also reported a decrement in the H_2 generation rate for Co-B powder when annealed above 573 K and the authors discussed the results in terms of the crystallization of Co metal. However, our present results indicate that even after crystallization of the Co

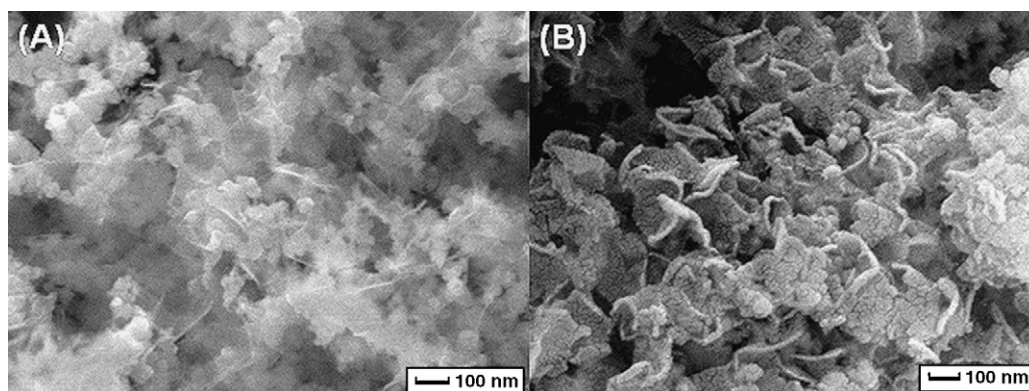


Fig. 9. SEM micrographs of Co-Ni-B ($\chi_{\text{Co}}=0.85$) catalyst powder (A) untreated and (B) treated in Ar gas atmosphere at 773 K for 2 h.

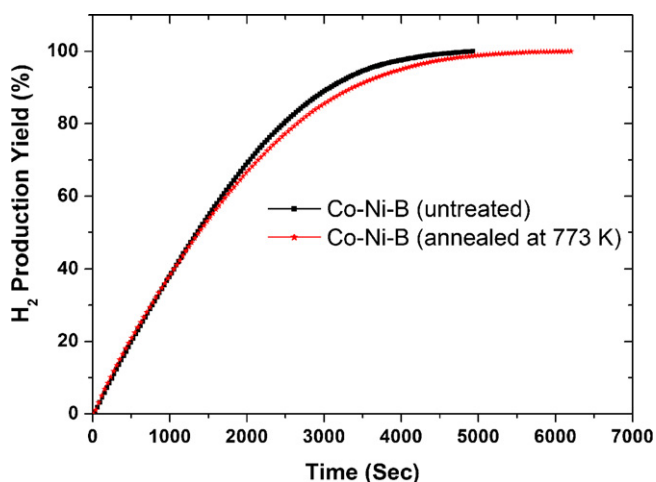


Fig. 10. Hydrogen generation yield as a function of reaction time with Co-Ni-B ($\chi_{\text{Co}} = 0.85$) catalyst powder untreated and heat-treated at 773 K obtained by hydrolysis of alkaline NaBH_4 (0.025 M) solution.

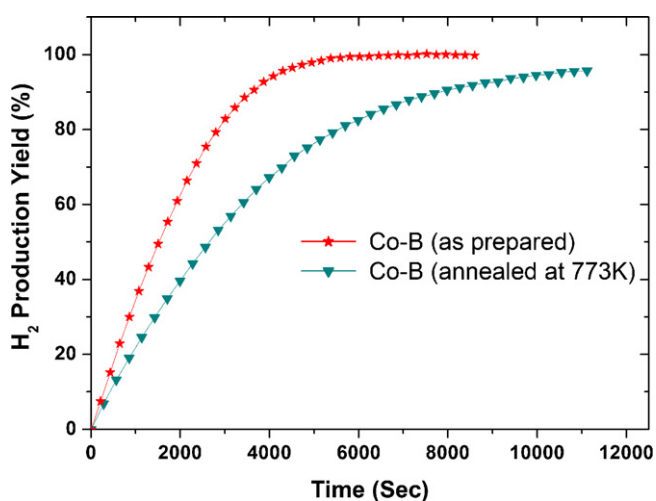


Fig. 11. Hydrogen generation yield as a function of reaction time with Co-B catalyst powder untreated and heat-treated at 773 K obtained by hydrolysis of alkaline NaBH_4 (0.025 M) solution.

metal phase in Co-Ni-B powder, the same powder maintains its catalytic efficiency. Thus it shows that the Co-Ni-B catalyst is stable and useful for high temperature application.

4. Conclusions

We have investigated the role of atomic composition in Co-Ni-B powder in the catalytic activity for hydrogen production by hydro-

lysis of NaBH_4 . It was proved that the presence of mixed Co-Ni with B atoms results in an enhanced catalytic effect with respect to Co-B or Ni-B powders. The effect is preserved after annealing of the Co-Ni-B powder and Co phase formation, as opposed to phase formation in Co-B powder. Possibly, transient electronic states are favoured with Co and Ni atoms in the Co-Ni-B powder that should be further investigated. In addition, surface morphologies as observed in Figs. 2B and 9, which are different from that pertinent to Co-B and Ni-B, could constitute an additional key to explain the reported results.

Acknowledgements

We thank Nicola Bazzanella for SEM-EDS analysis and Cristina Armellini for XRD analysis. The research activity is financially supported by the Hydrogen-FISR Italian project.

References

- [1] J.M. Ogden, T.G. Kreutz, M.M. Steinbugler, *Fuel Cell. Bull.* 3 (16) (2000) 5–13.
- [2] A.L. Dicks, *J. Power Sources* 61 (1996) 113–124.
- [3] R.B. Biniwale, S. Rayalu, S. Devotta, M. Ichikawa, *Int. J. Hydrogen Energy* 33 (2008) 360–365.
- [4] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, *J. Power Sources* 85 (2000) 186–189.
- [5] U.B. Demirci, F. Garin, *J. Mol. Catal. A: Chem.* 279 (2007) 57–62.
- [6] J. Lee, K.Y. Kong, C.R. Jung, E. Cho, S.P. Yoon, J. Han, T. Lee, S.W. Nam, *Catal. Today* 120 (2007) 305–310.
- [7] H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hockstra, E.K. Hyde, *J. Am. Chem. Soc.* 75 (1953) 215–219.
- [8] 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.
- [9] S. Suda, Y.M. Sun, B.H. Liu, Y. Zhou, S. Morimitsu, K. Arai, N. Tsukamoto, M. Uchida, Y. Candra, Z.P. Li, *Appl. Phys. A: Mater. Sci. Process* 72 (2001) 209–212.
- [10] Y. Bai, C. Wu, F. Wu, B. Yi, *Mater. Lett.* 60 (2006) 2236–2239.
- [11] G. Guella, C. Zanchetta, B. Patton, A. Miotello, *J. Phys. Chem. B* 110 (2006) 17024–17033.
- [12] P. Krishnan, T.H. Yang, W.Y. Lee, C.S. Kim, *J. Power Sources* 143 (2005) 17–23.
- [13] B.H. Liu, Z.P. Li, S. Suda, *J. Alloys Compd.* 415 (2006) 288–293.
- [14] S.U. Jeong, E.A. Cho, S.W. Nam, I.H. Oh, U.H. Jung, S.H. Kim, *Int. J. Hydrogen Energy* 32 (2007) 1749–1754.
- [15] N. Patel, G. Guella, A. Kale, A. Miotello, B. Patton, C. Zanchetta, L. Mirengi, P. Rotolo, *Appl. Catal. A: Gen.* 323 (2007) 18–24.
- [16] N. Patel, R. Fernandes, G. Guella, A. Kale, A. Miotello, B. Patton, C. Zanchetta, *J. Phys. Chem. C* 112 (2008) 6968–6976.
- [17] H. Li, Y. Wu, Ying Wan, J. Zhang, W. Dai, M. Qiao, *Catal. Today* 93 (2004) 493–503.
- [18] H. Li, Y. Wu, J. Zhang, W. Dai, M. Qiao, *Appl. Catal. A: Gen.* 275 (2004) 199–206.
- [19] J.C. Ingersoll, N. Mani, J.C. Thenmozhiyal, A. Muthaiah, *J. Power Sources* 173 (2007) 450–457.
- [20] D.A. Lyttle, E.H. Jensen, W.A. Struck, *Anal. Chem.* 24 (1952) 1843–1844.
- [21] C. Zanchetta, B. Patton, G. Guella, A. Miotello, *Meas. Sci. Technol.* 18 (2007) N21–N26.
- [22] J. Shen, Y. Chen, *J. Mol. Catal. A: Chem.* 273 (2007) 265–276.
- [23] W.L. Dai, M.H. Qiao, J.F. Deng, *Appl. Surf. Sci.* 120 (1997) 119–124.
- [24] A. Lebugle, U. Axelsson, R. Nyholm, N. Martensson, *Phys. Scr.* 23 (1981) 825–827.
- [25] H. Li, H. Li, W.L. Dai, Z. Fang, J.F. Deng, *Appl. Surf. Sci.* 152 (1999) 25–34.
- [26] H. Li, Y. Wu, H. Luo, M. Wang, Y. Xu, *J. Catal.* 214 (2003) 15–25.
- [27] S. Yoshida, H. Yamashita, T. Funabiki, T. Yonezawa, *J. Chem. Soc. Faraday Trans.* 1, 80 (1984) 1435–1446.
- [28] C.M. Kaufman, B. Sen, *J. Chem. Soc., Dalton Trans.* 2 (1985) 307–313.
- [29] C. Wu, F. Wu, Y. Bai, B. Yi, H. Zhang, *Mater. Lett.* 59 (2005) 1748–1751.