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Durability and reutilization capabilities of a Ni–Ru catalyst for the hydrolysis of sodium borohydride in batch reactors

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ABSTRACT

The study of catalyst durability and reutilization on catalyzed hydrolysis of sodium borohydride is essential from an application point of view. Few works on this topic are available in the literature. In the present work, a powder nickel–ruthenium based catalyst, unsupported, used in two different schemes of $NaBH_4$ hydrolysis (*alkaline* and *alkali free* hydrolysis), performed in batch reactors with different volumes and bottom geometries (flat and conical), was investigated in terms of durability and reutilization capabilities, throughout 300 cycles. For the *alkaline* $NaBH_4$ hydrolysis, the H_2 generation rate progressively decreases with catalyst reused and only ~25% of the initial H_2 generation rate remains after 300 reutilizations. For similar periods of catalyst aging, it was observed that the reactor conical bottom shape greatly enhances the H_2 generation rate (and practically eliminates the reaction induction time) in the solid or *alkali free* $NaBH_4$ hydrolysis, and, as a result, the values obtained for the H_2 generation rates, even after 300 extensive cycling, are above the range of the greatest values reported so far in the open literature. The catalyst, before and after 300 reutilizations, was characterized by textural properties based on nitrogen adsorption isotherms; by surface morphology using scanning electron microscopy (SEM) coupled with EDS spectroscopy and by X-ray photoelectron spectroscopy (XPS). The deterioration of the catalyst seems to be caused by ruthenium segregation from the Ni–Ru alloy, which brought to diminishing the catalyst performance throughout its 300 long-life reutilizations. Nevertheless, the capability of reutilization of the developed nickel-based bimetallic catalyst is a major finding bearing in mind the possible application of this concept for hydrogen generation and storage. The present work gives emphasis to the importance of considering different schemes of $NaBH_4$ hydrolysis in the study of catalyst durability and calls for increased caution in considering the reactor bottom geometry in those schemes.

1. Introduction

When considering the future of the Earth, as a whole and of its various regions, the deciding factor in terms of ecological sustainability is first and foremost the kind of energy carrier that is being mainly used by humankind.

The main energy sources used today are still fossil carbon fuels, namely, coal, oil, natural gas and products of their processing [1]. In fact, our dependence on fossil fuels and the problems associated with oil drop, global warming and pollution, are important drivers to find alternative and clean renewable energy carriers. In this perspective, hydrogen (H_2) is presented as an environmental friendly energy vector because it can be produced from water and renewable energy sources as well as from chemical hydrides. Hydrogen can be fed straight into a proton exchange membrane (PEM) fuel cell (FC), which is a device for direct conversion of a fuel chemical energy into electric energy, producing only water as a by-product. From an environmental point of view this is a great benefit for reducing air pollution.

Defenders of a “hydrogen economy” stated that in a near future a gradual transition to hydrogen powdered vehicles will be imposed and the concept of distributed production will be a reality. Therefore, a reliable hydrogen fuelling system needs to be developed. Taking into account the current problems associated with hydrogen storage (high cost, low mass density, the need for a distribution network, etc.), the on-board H_2 production and storage from, for example, chemical hydrides, seems a reasonable option for achieving CO_2-free transport system or even another niche applications, like portable computers, iPods, cellular phones, etc.

Chemical hydrides are materials that produce hydrogen ‘on-demand’ through a chemical reaction with water; and generally, they exhibit high gravimetric energy densities and are stable dur-

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ing long periods of storage without usage. Among the chemical hydrides, sodium borohydride ($NaBH_4$) has the advantage of storing hydrogen in a stable and safe solution. Its hydrogen content is 10.6 wt%, making it one of the highest hydrogen containing compounds (actually, $NaBH_4$ and ammonia-borane, NH_3BH_3, are appointed as the chosen hydrogen carriers for mobility by virtue of their high gravimetric/volumetric storage capacities, [2]). $NaBH_4$ reacts with water to generate molecular hydrogen according to the hydrolysis reaction (1):

$$NaBH_4 + (2 + x)H_2O \rightarrow NaBO_2{\cdot}xH_2O + 4H_2 + \text{heat} \qquad (1)$$

where x is the hydration factor. Ideal hydrolysis is attained for $x = 0$ [3], where two moles of water are required to react with one mole of solid $NaBH_4$ to liberate four moles of hydrogen, but in practice excess of water is necessary to account for the fact that the solid by-product ($NaBO_2{\cdot}xH_2O$) can exist with varying degrees of hydration [4]. In fact, most schemes for hydride hydrolysis require a large excess of water to pre-dissolve the hydride for storage or to keep the by-products in solution. Experimental studies showed that if the excess hydration factor is less that 2 ($x < 2$), unreacted hydride remains; but if $x > 2$ there is enough water for complete reaction and hydration of the borate.

On the other hand, at temperatures not so far from room temperature, the H_2 generation rate is not satisfactory without the presence of some catalysts. Schlesinger et al. [3] recognized the particular striking catalytic effect of certain transition metals and their salts on sodium borohydride hydrolysis rate. In truth, several metal catalysts enhance hydrolysis of the alkaline $NaBH_4$ solution, giving high-performance H_2 generation rates. Demirci and Garin [5] and more lately Liu and Li [6] reviewed the most used catalysts in reaction (1). However, some critical problems in the development of hydrogen generation technology from $NaBH_4$ hydrolysis have been generally stated [2,4,6,7]. Catalyst degradation is a very well known difficulty. Agglomeration of catalyst particles, surface oxidation of catalyst and catalyst component dissolution in alkaline $NaBH_4$ solutions are common reasons for catalyst deterioration. Also, the strong generation of hydrogen bubbles in the liquid phase promotes shocks between catalyst particles that can contribute to damage the material, particularly for high H_2 production rates [6]. The US DOE set technical targets for durability and operability of catalysts, but the reasoning behind the targets set was not explained in their review [8].

In fact, the deterioration of the catalyst activity is an extremely important issue, since the catalyst is the *key* material for varying the amount of generated molecular hydrogen from $NaBH_4$ hydrolysis reactions. Most of the published work, since the late 1990s, was devoted to the study of the catalyst reactivity and very few papers studied the catalyst durability and reutilization. Indeed, the durability studies are actually quite recent and just a few researches on the subject could be found in the open literature.

Kim et al. [9] studied the degradation of filamentary Ni catalyst upon hydrolysis of $NaBH_4$ and reported, after 200 cycles of hydrogen generation (HG), a decrease of 76% on the initial hydrogen generation rate (HGR) due to the deterioration of the catalyst. By analysing the catalyst surface prior and after the cycling tests, those authors observed that the catalyst agglometated which brought to diminishing of the catalyst specific surface area and so to the catalyst reactive sites. Additionally, a deactivating film spreading the catalyst surface was registered with cycling. This film consisted of $Na_2B_4O_7{\cdot}10H_2O$, potassium borate (KB_xO_y) and boron oxide (B_2O_3). It was concluded that the deterioration of the catalyst upon the catalytic hydrolysis of $NaBH_4$ results from both agglomeration and film formed at the catalyst surface.

Zhang et al. [10] studied the durability of a supported catalyst by measuring, at a steady-state operation, the flow reactor under a liquid $NaBH_4$ fuel, hourly space velocity (LHSV) of 15 h^{-1} at 483 kPa. A fuel conversion over 92% was achieved over more than 700 h time-on-stream operation.

Peña-Alonso et al. [11] reported that 300 L min^{-1} $g_{metal}{}^{-1}$ $[NaBH_4]^{-1}$ had been achieved from stabilized $NaBH_4$ solutions with Pt and Pd atoms dispersed elementally on functionalized surfaces of carbon nanotubes, and concluded that the catalyst is robust, showing negligible degradation even after more than 20 experimental cycles.

Keçeli and Özkar [12] applied a procedure similar to that applied by Kim et al. [9] for testing the durability of their ruthenium (III) acetylacetonate catalyst. At 25 °C and for a 150 mM sodium borohydride solution with [Ru] = 1.0 mM, 1200 turnovers over 180 min in HG, from hydrolysis of $NaBH_4$, was registered before the catalyst deactivation.

Krishnan et al. [13,14] proposed a different approach. Cobalt boride (Co_2B) catalysts, formed *in situ* from various cobalt oxide precursors, for extended HG operation, were studied for durability in a 1000 mL capacity tubular reactor with $NaBH_4$ 10 wt% (5 wt% NaOH) solution. Co_2B–Co_3O_4 [13] was tested over a period of 25 h and the HGR remained more or less steady at around 125 mL/min for the first 20 h and declined subsequently when all of the $NaBH_4$ present in the solution was hydrolysed. A CoB–Ni catalyst [14] was also tested for extended duration of up to 60 h and the HGR decreased within 5 min and then it remained almost constant.

Komova et al. [15] reported on fourteen cyclic stability tests for $LiCoO_2$-3 and modified 1%Rh/$LiCoO_2$-3 and 1%Pt/$LiCoO_2$-3 catalysts at 40 °C (0.0117 g being the catalyst weight) for HG from one $NaBH_4$ portion (0.0465 g dissolved in 10 mL of distilled water). The results showed that the catalyst activity quickly declines and this effect is most likely caused by degradation of the surface of lithium cobaltite particles. They concluded that the impregnation of lithium cobaltite with either Rh or Pt chlorides is not beneficial, since the active component in the studied catalyst is formed *in situ* in the $NaBH_4$ reaction medium.

Other authors applied one to six cycles for testing the durability of their respective catalysts [16–22] and, in each case, almost the same catalytic activities as fresh catalyst were obtained during cyclic usage. Whatever the experimental conditions and the nature of the catalyst used in each study, it is certain that the durability tests were too superficial.

At this stage it can be concluded that from an application point of view the durability of the catalyst is as well important as its reactivity. Consequently, the stability of catalysts during long operating period for successive HG needs to be systematically studied and the experiments should also enclose severe testing/operating conditions [7].

Other important issues regarding to hydrolysis of $NaBH_4$, are the refueling of fresh solution, which is directly related to the storage system, the design of the reactor and the possibility of storage H_2 in the liquid phase by changing the polarity of the *fuel* with an organic additive. In previous works [23–25], the authors discussed these issues which were found scarce, sometimes inexistent, throughout the open literature.

In the present work, the durability and reutilization capabilities of a powdered nickel based bimetallic catalyst are exposed, and the approaches for elucidating the degradation mechanism of the catalyst, after 300 reutilizations, on the hydrolysis of $NaBH_4$ in batch reactors, are for the first time reported.

2. Experimental

The catalyst used in all the experiments reported by the authors [23–27] is a nickel–ruthenium based catalyst in the form of a finely divided black powder, unsupported. The catalyst was prepared in April of 2008 from a mixture of precursors in deionised water – impregnating small quantities of ruthenium in the nickel salts (Riedel-de Haën) – by chemical reaction with 10 wt% stabilized borohydride solution (Rohm and Haas), as the reducing environment. When the reduction was complete the catalyst was appropriately decanted, washed, filtered, dried and heat-treated at 110 °C. The catalyst was kept in a desiccator until use.

The hydrogen generation experiments, made since the synthesis of the catalyst and reaching the impressive number of 300 reutilizations, involved different proportions of Ni–Ru based catalyst/$NaBH_4$, in the range of 0.1 g/g to 0.6 g/g, and were done through three different schemes of hydrolysis, namely: (a) *alkaline hydrolysis* using stabilized reactant aqueous solutions of $NaBH_4$ (5, 10, 15, 20, 25, 30 and 40 wt%) and NaOH (1, 3, 7, 10, 20 and 30 wt%), (b) *alkali free* hydrolysis, adding a stoichiometric amount of water molecules, $H_2O/NaBH_4$ (mol/mol), from molar ratios 2 to 8, to hydrolyze solid $NaBH_4$ (in order to produced H_2 with higher storage capacities), and (c) *less Polar Organic Polymeric Solutions (lPOPS)* hydrolysis, adding small quantities of an organic polymer to the $NaBH_4$ plus NaOH reactant solution (in order to increase the affinity to storage the generated H_2 in the liquid phase remaining inside the reaction vessel). The sodium borohydride powder (96% purity, anhydrous) was provided by MERCK (No.: 1.06371.0100) and stored in a dessicator until use; and the sodium hydroxide (98% purity) was supplied by EKA (No.: 1310.73.2). Deionised water was used to prepare the aqueous reactant solutions and, in all of them, the initial pH was approximately 14.

The above mentioned catalytic hydrolysis schemes were performed in batch reactors, under moderate pressures (of up to 3 MPa), made in stainless steel, with three different internal volumes (LR/0.646 mL, MR/0.369 mL and SR/0.229 mL) and two different bottom geometries (flat and conical); with temperature control (15, 20, 25, 30, 35, 45 and 55 °C) and also at ambient uncontrolled conditions, and with and without magnetic stirring.

Successive loadings of stabilized reactant solution, in which the amount of catalyst is kept constant during the refueling process, were also experimented.

The effects of (i) operating pressure (using batch reactors with different internal volumes and bottom geometries), (ii) $NaBH_4$ concentration, (iii) NaOH concentration, (iv) temperature; (v) magnetic stirring, (vi) stoichiometric amount of added water molecules (in the *alkali free* hydrolysis), (vii) small addition of an organic polymer to the reactant solution (in the *lPOPS* hydrolysis), (viii) successive refueling (keeping constant the amount of catalyst inside de reactor), (ix) sudden valve opening (before reaction completion) on H_2 generation rates, yields and induction time, were investigated through different catalyst “ages” [23–27]. It is worth to emphasize that the same amount of catalyst was reused around 300 times (between the experiments, the used Ni–Ru based catalyst was separated by sedimentation from the by-product slurry, washed five times with deionised water, dried at 60 °C for 3 h, and kept in a desiccator until next re-utilisation).

2.1. Selected hydrogen generation experiments

As already referred, the purpose of the present work is studying the aging of the Ni–Ru based catalyst, and consequently, the approaches for clarifying its degradation mechanism after 300 reutilizations. Therefore, HG experiments were selected to be presented at mainly two different stages of the catalyst reutilization: (i) a newer stage of up to 40 times reused and (ii) an older stage near the 300 reutilizations. Hence, particular experiments, in the presence of powder reused nickel-based bimetallic catalyst (in a proportion of catalyst/$NaBH_4$: 0.4 g/g), performed in the three tested batch reactors at room temperature (23–26 °C) and without magnetic stirring were carefully chosen. Some experiments with the *fuel* ($NaBH_4$) in the liquid form, used in *alkaline* hydrolysis (10 mL of the reactant solution – 10 wt% $NaBH_4$ – was stabilized by the addition of small quantities of sodium hydroxide pellets – 7 wt% NaOH – as a hydrolysis inhibitor) and some with the *fuel* in the solid state, used in *alkali free* hydrolysis (by adding a certain molar quantity of pure water, in the proportion of $H_2O/NaBH_4 = 4$ mol/mol). (*Note*: In all the *alkali free* hydrolysis experiments reported in this work, an amount of approximately 1.2 g of $NaBH_4$ was used for comparison with the results obtained in the *alkaline* hydrolysis, since in 10 mL of the reactant aqueous solution 10 wt% $NaBH_4$ plus 7 wt% NaOH, the amount of $NaBH_4$ is approximately 1.2 g.)

The temperature of the reactor medium was monitored by a k-thermocouple, named T.Top, and recorded with a data acquisition system using Labview software. To monitor the rate of hydrogen generation, using the same data acquisition system, the gas pressure inside the reactor was followed with an appropriate pressure transducer until attaining a constant pressure inside the reactor. Detailed description of the rig and of the experimental techniques can be found elsewhere [22–24].

2.2. Catalyst characterization

The catalyst surface states were analyzed prior and after the 300 times of reutilizations, in order to further elucidate the degradation mechanism of the Ni–Ru based catalyst throughout its long-life use. Morphology and elemental composition analysis of the catalyst were obtained with a Scanning Electron Microscopy (SEM) coupled with EDS unit FEI Quanta 400 FEG ESEM/EDAX Genesis X4 M operating at 15 kV in low vacuum mode (LVSEM for uncoated non-conductive sample). The powder sample was prepared by simple dispersion over a double side adhesive carbon tape. X-ray photoelectron spectroscopy (XPS) of the catalyst, after reducing the powder sample into a pellet of 10 mm diameter, was carried out on a VG Scientific ESCALAB 200 A spectrometer using Mg Kα (1,253.6 eV) as a radiation source.

The determination of surface areas (S_{BET}), by N_2 physisorption was undertaken at 77 K, using a Quantachrome Instruments Nova 4200e apparatus. Prior to the analysis, the samples (0.127 g) were degassed at 160 °C for 3 h. Pore size distributions were obtained from the desorption branch of the isotherms using the Barrett, Joyner and Halenda (BJH) method. The micropore volumes and mesopore surface areas were determined by the t-method.

The discussion of the results, next presented, will give emphasis to the importance of considering both different schemes of $NaBH_4$ hydrolysis and the reactor bottom geometry in the study of catalyst durability.

3. Results and discussion

3.1. Catalyst activity analysis in selected $NaBH_4$ hydrolysis experiments

As previously referred, the catalyst has been used since its synthesis in several studies [23–27]. The results obtained in two different schemes of $NaBH_4$ hydrolysis, performed at different catalyst “ages”, are next reported and compared.

3.1.1. Alkaline hydrolysis

Fig. 1 shows examples of hydrogen generating curves (H_2 pressure as a function of time), obtained in the *alkaline* hydrolysis (for one single injection of reactant solution), for two different catalyst ages and for the three reaction vessels LR/646 cm^3, MR/369 cm^3 and SR/229 cm^3, the latter two with conical bottom shape. As can be seen from the slope (dP/dt) of the curves (in the linear zone) of Fig. 1, the hydrogen generation rates in the two reactors with conical shaped bottom are substantially higher (0.034 bar/s and 0.056 bar/s, respectively, for MR and SR reactors in a newer stage of

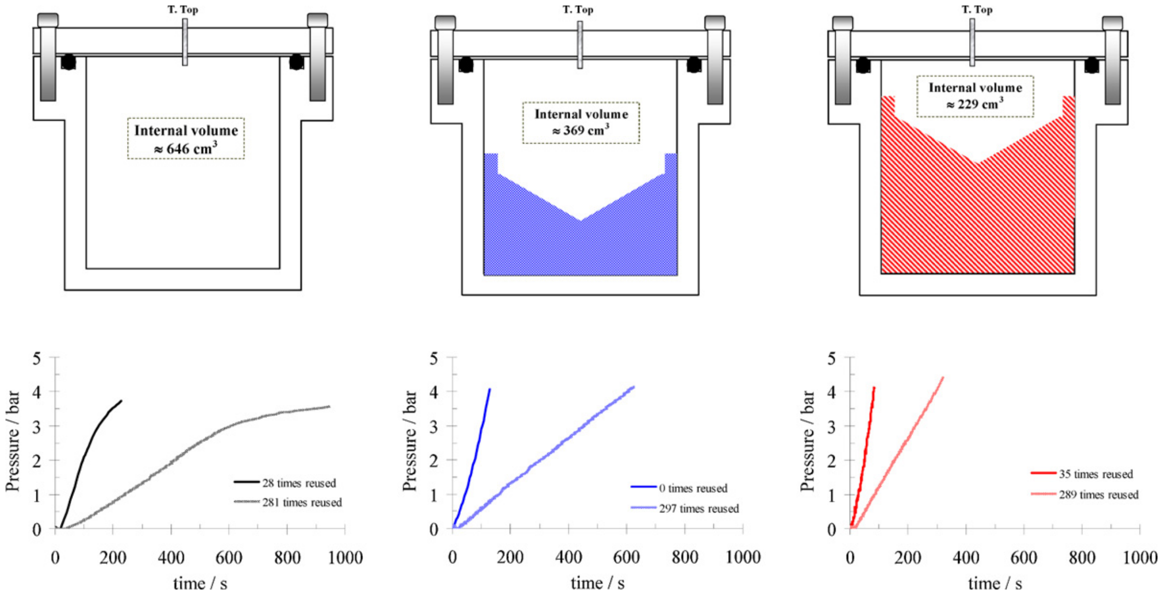

Fig. 1. Schematic view of the inside of the three batch reactors and hydrogen generation plots in (a) LR/646 cm^3, (b) MR/369 cm^3 and (c) SR/229 cm^3 reactors, with a $NaBH_4$ concentration of 10 wt% and an inhibitor concentration of 7 wt%, for two different stages of catalyst reutilization: a newer stage of 0–35 times used and a more older stage of 281–297 times used.

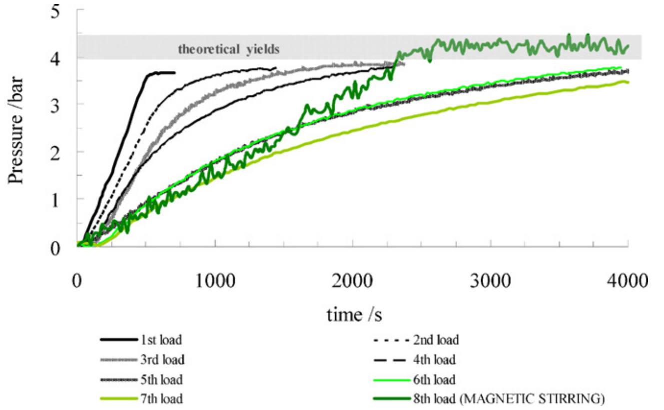

Fig. 2. Hydrogen generation in the batch reactor LR/646 cm^3 of eight successive loadings, of 10 mL each, of the reactant solution: 10 wt% $NaBH_4$, 7 wt% NaOH, 83 wt% H_2O, at room temperature (≈25 °C), with Ni–Ru based catalyst/$NaBH_4$ = 0.40 g/g reused 226–233 times (the 8th loading was performed with magnetic stirring).

the catalyst; in the LR reactor, the *dP*/*dt* being 0.023 bar/s), putting in evidence the positive influence of the bottom geometry on the hydrolysis performance. It is worth mentioning the remarkable performance of the catalyst 289 times re-used in the smaller reactor, SR/229 cm^3 (0.014 bar/s or 0.38 L(H_2) min^{-1} $gcat^{-1}$). In truth, the catalyst slowly looses performance but still exhibits hydrogen generation rates within the higher values found in the open literature [5–7]. The induction-times (here defined as the time required to obtain 0.5 bar in the H_2 generation pressure) are low for all the reported conditions.

3.1.1.1. Alkaline hydrolysis with successive loadings of reactant solution. During the *alkaline* hydrolysis studies, a set of experiments was performed with successive loadings of reactant solution, throughout a catalyst stage inferior to 50 times reused, without controlled reaction temperature and without stirring [23]. Hydrogen generation results of a much more aged catalyst, 226–233 times reused, subjected to eight successive loadings of *fuel*, performed in LR batch reactor, is for the first time presented in Fig. 2. In addition, magnetic stirring was allowed in eighth loading to investigate possible mass transfer limitations between the reacting solution and the reused catalyst.

As can be seen from the HG curves in Fig. 2, the magnetic stirring had a very positive impact on the hydrolysis performance, suggesting the minimization of mass transfer limitations between reacting solution and catalyst in the refueling process. Hence, the capability of re-use a constant amount of catalyst during successive loadings of *fuel*, without any treatment and without significant loss of activity, is a very important finding, plenty to be mentioned in the present manuscript. In fact, the reused Ni–Ru based catalyst kept very good activity in the successive reactions, the induction times are low and the hydrolysis reaches almost completion in short times [23].

3.1.2. Alkali free hydrolysis (or solid $NaBH_4$ hydrolysis)

Some examples of hydrogen generation curves are presented in Fig. 3 corresponding to the reaction of 1.2 g of $NaBH_4$ and $H_2O/NaBH_4$ = 4 mol/mol, with a proportion of Ni–Ru based catalyst/$NaBH_4$: 0.4 g/g and at room temperature (≈25 °C). The reactions were performed in the three reactors for different stages of catalyst reutilization (26, 112 and 266 times reused) with the objective of comparing simultaneously the effects of the reactor bottom shape and the catalyst aging on H_2 generation rate. The strong positive effect of the conical bottom shape both on the H_2 generation rate and induction time is again evident on the plots of Fig. 3. In particular, the curve obtained with the oldest catalyst (266 times reused) is remarkable, exhibiting a short lag time (18 s) and a very high H_2 generation rate (1.18 bar/s of *dP*/*dt* slope in the linear zone of the curve). A plausible explanation is that the reactor conical bottom shape deeply enhances the contact between the catalyst and $NaBH_4$ powder, and the injected distilled water. In fact, the experiment conducted in LR vessel, with a flat bottom, inhibiting a proper contact between the solids and water, showed a significant lower performance (0.0006 bar/s) and greater induction time (580 s).

3.1.3. Effect of catalyst aging on hydrogen generation rates

Table 1 depicts typical Hydrogen Generation Rates (HGR) reported in the open literature [5,28–33] and some values obtained with the Ni–Ru based catalyst along the several studies performed

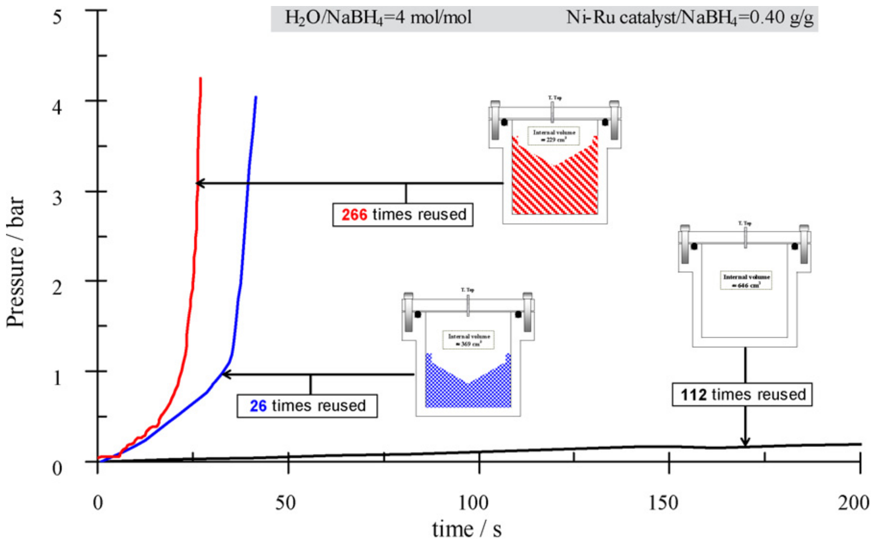

Fig. 3. Hydrogen generation plots obtained for the reaction of 1.2 g of $NaBH_4$ and $H_2O/NaBH_4$ = 4 mol/mol, with a proportion of Ni–Ru based catalyst/$NaBH_4$: 0.4 g/g and at room temperature (≈25 °C). The reactions were performed in the three batch reactors (LR/646 cm^3, MR/369 cm^3 and SR/229 cm^3) for different stages of catalyst reutilization (112, 26 and 266 times reused, respectively).

[24]. The values of the HGR, expressed as L(H_2)/(g catalyst min), obtained in the present work, compare extremely well with the most significant values found in the open literature even in the case of the lower values obtained (experiments with a more aged catalyst performed in the LR vessel). Remarkable values were obtained in the conical shaped reactors and in particular with the solid $NaBH_4$ hydrolysis (*alkali free*).

The HGR values, expressed in L(H_2)/(g active metal min), are significantly higher than the most higher values found in literature. It is important to recall that most of these works do not refer information on reutilization.

Fig. 4 summarizes the cyclic behavior on HGR for the Ni–Ru based catalyst (0.48 g or 12 wt%) in 10 wt% $NaBH_4$ alkaline solution (pH = 13.7) at room temperature. It is observed that the HGR progressively decreases with catalyst reused and only ∼25% of the initial HGR remains at ∼300 reutilizations. Similar results were obtained by Kim et al. [9], with a filamentary Ni catalyst. Those authors reported a decrease of 76% of the initial HGR after 200 cycles, performed in 14 wt% $NaBH_4$ alkaline solution (pH = 13).

Fig. 5 compares the catalyst performance in the two studied $NaBH_4$ hydrolysis schemes, for similar periods of catalyst aging. The results sketched in Fig. 5 put in evidence that the reactor bottom

Table 1
Hydrogen generation rates (HGR) reported in the open literature (approximate values) and comparison with the Ni–Ru based catalyst throughout long-life cycles.

Catalyst	Reused catalyst (number of times)	Hydrolysis configuration[a]		Temperature (°C)	H_2 yield (%)	H_2 rate, L(H_2) min^{-1} g^{-1} (catalyst)	H_2 rate, L(H_2) min^{-1} g^{-1} (active metal)	Reference
		$NaBH_4$ (wt%)	NaOH (wt%)					
5 wt% Ru dispersed on IRA 400 resin	N.C.	20	10	25–55	N.C.	0.199	3.98	[28]
5 wt% Ru dispersed on IRA 400 resin	N.C.	7.5	1	0–40	N.C.	0.378	7.56	[29]
10 wt% PtRu–$LiCoO_2$	N.C.	5	5	25	N.C.	1.2	12.4	[30]
Ru(0) nanoclusters	N.C.	0.57	0	30–45	N.C.	3.65	3.65	[31]
Ru	N.C.	20	5	20	N.C.	1.6	1.6	[32]
5 wt% Ru–C	N.C.	0.993	3.75	25	N.C.	0.7	12.9	[33]
1 wt% Ru_2Pt_1–TiO_2	N.C.	2	4	20	N.C.	0.15	15.2	[5]
0.48 g (or 12 wt%) Ni–Ru based; SR	∼150	30	0	22	98	26	1841[b]	[24]
Alkaline hydrolysis (x = 16)								
LR (646 cm^3); flat bottom								
0.48 g (or 12 wt%) Ni–Ru based	28	10	7	25	100	1.81	67[b]	Present study
0.48 g (or 12 wt%) Ni–Ru based	281	10	7	25	100	0.47	16[b]	Present study
MR (369 cm^3); conical bottom								
0.48 g (or 12 wt%) Ni–Ru based	0	10	7	25	100	1.61	54[b]	Present study
0.48 g (or 12 wt%) Ni–Ru based	297	10	7	25	100	0.30	11[b]	Present study
SR (229 cm^3); conical bottom								
0.48 g (or 12 wt%) Ni–Ru based	35	10	7	25	100	1.63	55[b]	Present study
0.48 g (or 12 wt%) Ni–Ru based	289	10	7	25	100	0.38	14[b]	Present study
Alkali free hydrolysis (x = 2)								
0.48 g (or 12 wt%) Ni–Ru based; LR	112	30	0	25	78	0.05	3[b]	Present study
0.48 g (or 12 wt%) Ni–Ru based; MR	26	30	0	25	86	22	1549[b]	Present study
0.48 g (or 12 wt%) Ni–Ru based; SR	266	30	0	25	96	33	2336[b]	Present study

N.C. = non-communicated.

[a] The wt% refers to the component content in aqueous solution.

[b] The active metal considered in the reused Ni–Ru based catalyst was the ruthenium, with the atomic concentration of 1.74 at.%.

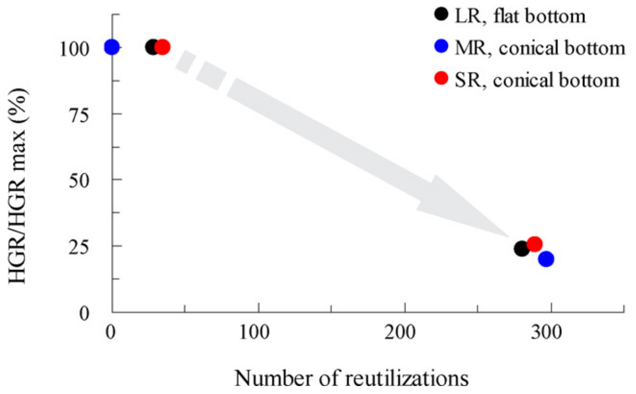

Fig. 4. Cyclic behavior on H_2 generation rate (HGR) for the Ni–Ru based catalyst (0.48 g or 12 wt%) in 10 wt% $NaBH_4$ alkaline solution (pH = 13.7) at room temperature (~25 °C).

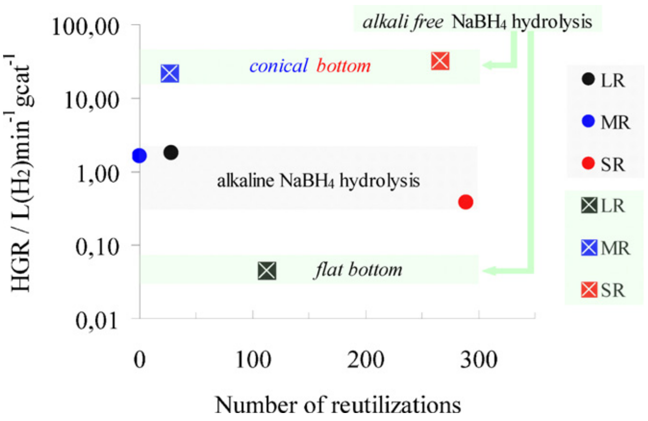

Fig. 5. Catalyst performance in the two studied $NaBH_4$ hydrolysis schemes (*alkaline* and *alkali free*), for related periods of Ni–Ru based catalyst aging, at room temperature (~25 °C).

geometry clearly influences the HGR regarding to the type of catalytic $NaBH_4$ hydrolysis: the conical bottom shape greatly enhances the HGR (and practically eliminates the reaction induction time) in the solid $NaBH_4$ hydrolysis or *alkali free* $NaBH_4$ hydrolysis.

To conclude, the present results give emphasis to the importance of considering different schemes of $NaBH_4$ hydrolysis in the study of catalyst durability and calls for increased caution in considering the reactor geometry in those studies.

3.1.4. Effect of catalyst aging on gravimetric and volumetric hydrogen storage capacities

The main purpose of exploring the path *alkali free* hydrolysis for H_2 generation from sodium borohydride, reported in Section 3.1.2, is to generate H_2 at high rates with very high Gravimetric Hydrogen Storage Capacity (GHSC) and Volumetric Hydrogen Storage Capacity (VHSC). In fact, it is commonly accepted [4,7,24] that the ability to work with ideal hydrolysis, i.e., with $x = 0$, and produce anhydrous sodium borate or less hydrated by-products are the key to increase the overall storage density of systems based on sodium borohydride as the storage media.

Table 2 presents the US DOE FreedomCAR 2007–2010–2015 targets [8] and a summary of the highest effective values of GHSC and VHSC reported so far in the open literature [4,34,35]. However, those values do not take into account the storage system as a whole. If this was done, then the given effective capacities would have been much lower (the given capacities must be divided by a factor of around 2) and none of the outlined $NaBH_4$ storage solutions would meet the 2010–2015 targets. The VHSC for the systems studied in the present work was calculated by adding the densities of $NaBH_4$ (1.07 g/cm^3), water (1.00 g/cm^3; or of stabilized aqueous solution) and of Ni–Ru based catalyst (3.17 g/cm^3), i.e., based on the density of the *materials-only*. It was found, for example, for $x = 2$, in the SR batch reactor, significant effective values for GHSC and VHSC, respectively, 6.1 wt% and 66 kg m^{-3}. Accordingly, one can admit the no-go recommendation for $NaBH_4$ for on-board vehicular hydrogen storage, but the present results (for $x = 2$, in SR reactor) shows that our compressed system is suitable for H_2 storage for portable and/or niche applications, for which the specifications are less severe: GHSCs of 3–7% are acceptable [36].

For the experiments with x in excess ($x = 16$), much lower values were found for GHSC and VHSC, respectively, 2.1 wt% and 23–24 kg m^{-3} (the H_2 yield being 100%) for the *alkaline* $NaBH_4$ hydrolysis, with the catalyst reused between 0 and 297 times.

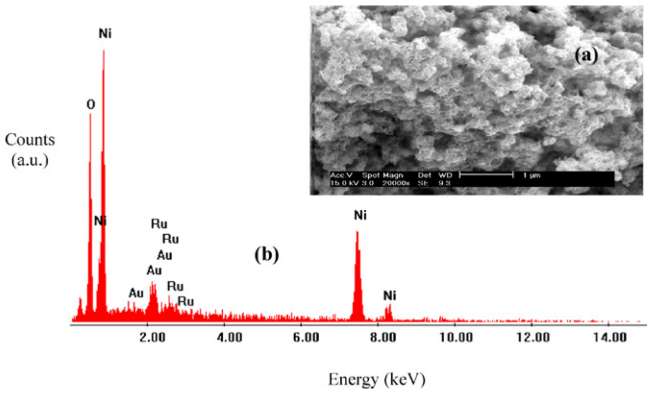

Fig. 6. SEM micrograph view of the synthesized Ni–Ru based catalyst powder (a) and associated elemental EDS spectrum (b).

3.2. Catalyst characterization

The degradation mechanism of the powdered Ni–Ru based catalyst on the hydrolysis of $NaBH_4$ through the two mentioned schemes – *alkaline* and *alkali free* hydrolysis – is still not understood, and so attempts have been made to clarify the deterioration mechanism for the studied bimetallic catalyst through SEM, XPS and BET analysis.

3.2.1. Segregation of ruthenium on catalyst

Fig. 6 shows SEM image and the corresponding EDS spectrum of the *fresh* Ni–Ru based catalyst (before use in the $NaBH_4$ hydrolysis studies).

The SEM micrograph (Fig. 6a) shows a homogenous ruthenium distribution and the EDS spectrum shows a very small amount of Ru as part of the catalyst composition. The amount of ruthenium present in the fresh catalyst is very small and was not always detectable by EDS, however a concentration under one atomic percent (0.74 at.%) was obtained by XPS.

Fig. 7 shows SEM micrographs of the powder Ni–Ru based catalyst after 300 times reused. Going from Fig. 7(a)–(e), the magnetic properties of Ni–Ru based appear to cause some agglomeration of the smaller particles. Therefore, closer examination of the particles surface in Fig. 7(c) shows a finer reticulated structure, interconnecting more or less spherical particles (like *microspheres*). Departing from Fig. 7(d) to (e), it may be assumed that these *microspheres* formed a three-dimensional structure (images at higher magnification showed distortions due to slight magnetic properties of the catalyst sample).

Fig. 8 shows a SEM image coupled with EDS spectra of the Ni–Ru based catalyst (300 times reused), in three different areas of the catalyst sample, at a specific magnification of 10,000×. The EDS

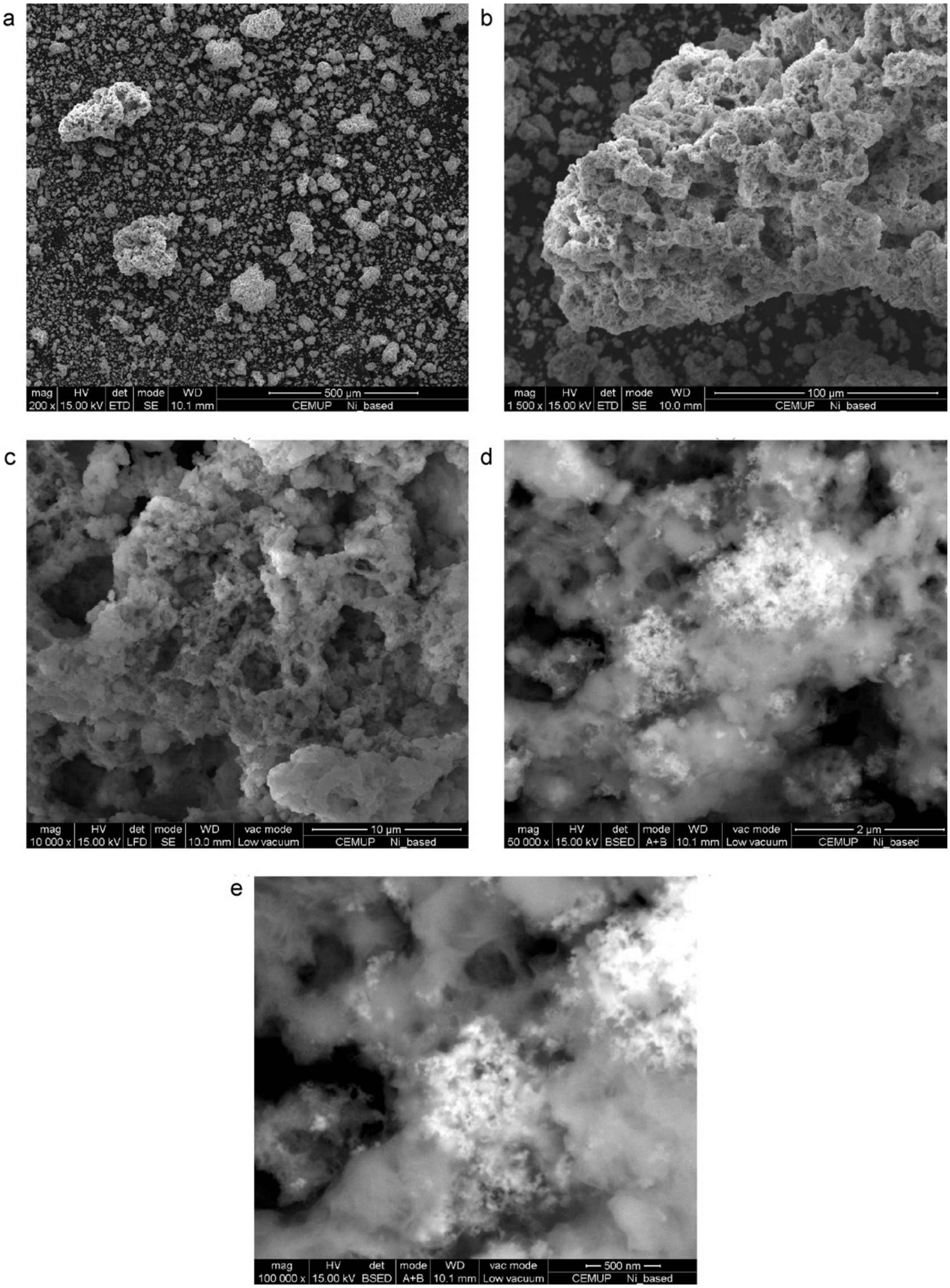

Fig. 7. SEM micrographs of powder Ni–Ru based catalyst, 300 times reused. Magnifications between 200× and 100,000×, increasing from (a) to (e).

spectra show that nickel is the main constituent and the amount of ruthenium element depends directly on the magnitude of the surface area selected to EDS analysis. In fact, for particular E2, E3 and E4 areas, the corresponding EDS spectra have shown different quantities of Ru.

The SEM results envisage that the deterioration of the catalyst could be attributed to the ruthenium segregation on the catalyst surface. In fact, the SEM images showed a more homogeneous Ru distribution for the fresh catalyst (see Fig. 6), even though the amount detected is very small, falling sometimes below the detection limit of EDS. However, Ru-rich areas were evident in the 300 times reused catalyst sample, as can be seen in Fig. 8. These results give emphasis that local increase in the amount of Ru due to segregation has occurred on the catalyst surface after 300 of reutilizations.

In order to further elucidate the deterioration mechanism of the catalyst, XPS analysis were performed to study the chemical changes in the surface of the Ni–Ru based catalyst before and after 300 cycles. For this analysis, an achromatic Al (Kalfa) X-ray source operating at 15 kV (300 W) was used, and the spectrometer, cali-

Table 2
Gravimetric and volumetric hydrogen storage capacities (GHSC and VHSC, respectively) and comparison with the Ni–Ru based catalyst throughout the long-life cycles.

	Reused catalyst[a]	GHSC (wt%)	VHSC (kg(H_2) m^{-3})	Reference
US DOE FreedomCAR targets				
2007 target	–	4.5	36	[8]
2010 target	–	6.0	45	[8]
2015 target	–	9.0	81	[8]
Highest effective capacities reported in the open literature[b]				
$NaBH_4$ (aqueous stabilized solution)	N.C.	6.7	80	[34]
$NaBH_4$ (solid; liquid water provided)	N.C.	9.0	188	[35]
$NaBH_4$ (solid; vapour water provided)	N.C.	N.C.	N.C.	[4]
$NaBH_4$ (solid; liquid water provided, $x = 2$)[a,c] SR	~150	6.3	70	[24]
$NaBH_4$ (solid; water provided from a stabilized solution with 0.25 wt% CMC, $x = 0$)[a,c] SR	~277	5.5	61	[25]
Effective capacities in the present work, *alkaline hydrolysis*[a]				
$NaBH_4$ (aqueous stabilized solution, $x = 16$); LR (646 cm^3, flat bottom)	28	2.1	23	Present study
	281	2.1	23	Present study
$NaBH_4$ (aqueous stabilized solution, $x = 16$); MR (369 cm^3, conical bottom)	0	2.1	24	Present study
	297	2.1	24	Present study
$NaBH_4$ (aqueous stabilized solution, $x = 16$); SR (229 cm^3, conical bottom)	35	2.1	23	Present study
	289	2.1	23	Present study
Effective capacities in the present work, *alkali free hydrolysis*[a]				
$NaBH_4$ (solid; liquid water provided, $x = 2$); LR (646 cm^3, flat bottom)	112	5.0	55	Present study
$NaBH_4$ (solid; liquid water provided, $x = 2$); MR (369 cm^3, conical bottom)	26	5.3	58	Present study
$NaBH_4$ (solid; liquid water provided, $x = 2$); SR (229 cm^3, conical bottom)	266	6.1	66	Present study

N.C. = non-communicated; x represents the excess hydration factor.

[a] Ni–Ru based catalyst, in the present work and other published work by the authors.

[b] Without considering the net storage system.

[c] Experiments performed in the batch reactor SR (229 cm^3).

brated with reference to C1 s (285 eV), was operated in CAE mode with 20 eV pass energy. Data acquisition was performed with a pressure lower than 1E−6 Pa. Spectra analysis was performed using peak fitting with Gaussian–Lorentzian peak shape and Shirley type background subtraction (or linear taking in account the data).

Fig. 9 shows a comparison, for catalyst samples before and after use, of the survey XPS spectra of the studied samples. A small amount of Na and B was detected, the latter more evident in the fresh catalyst sample even though the peak, at 193 eV, presents a very low intensity. The referred peak may be adjudicated to a B–O

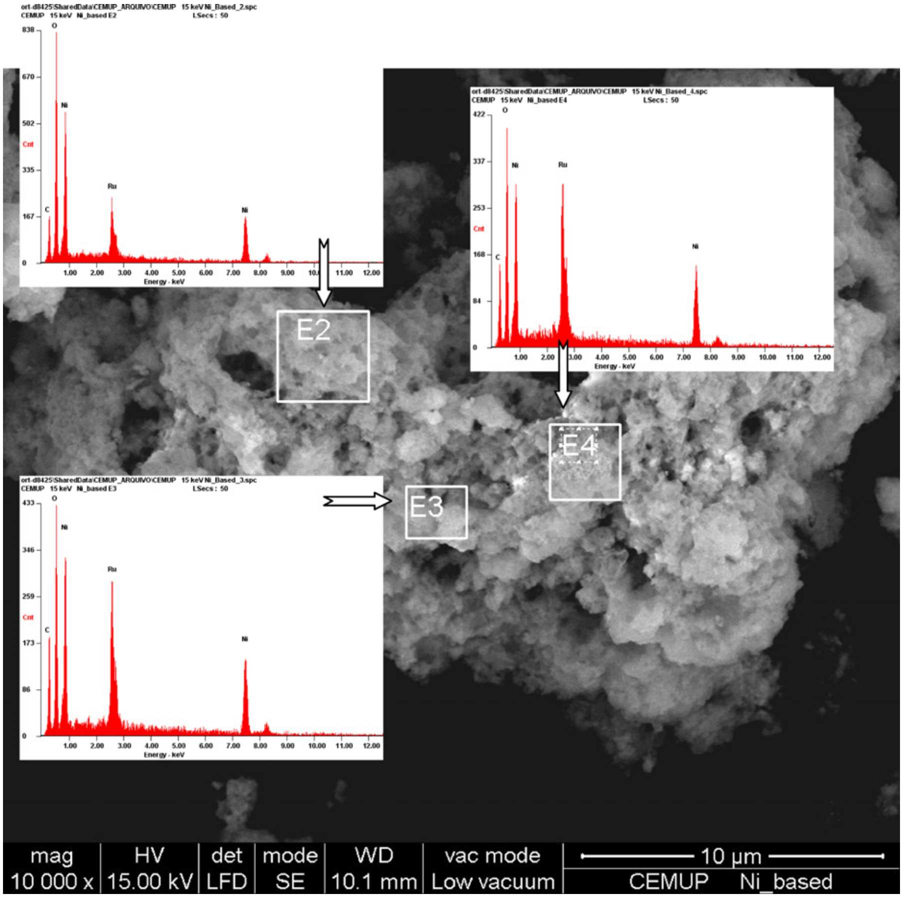

Fig. 8. SEM image coupled with EDS spectrum, at three different selected areas, of the Ni–Ru based catalyst 300 times reused and a magnification of 10,000×.

Table 3
Results of XPS analysis of Ni–Ru based catalyst 300 times reused.

Element	Peak range	Area	Sens. factor	at.%
C 1s	Synthesis	13,285	1	13.57
O 1s	Synthesis	187,038	2.93	65.20
Ni 2p3	Synthesis	283,316	14.61	19.81
Ru 3d5	Synthesis	10,269.3	7.39	1.42

at.% = atomic concentration, in %.

Table 4
Textural properties of the Ni–Ru based powder catalyst used in the present study, before and after 300 re-utilizations.

Catalyst	S_{BET} ($m^2\,g^{-1}$)	V_{μ} ($cm^3\,g^{-1}$)	S_{ext} ($m^2\,g^{-1}$)	V_p ($cm^3\,g^{-1}$)
Before use	54	0	52	0.22
After 300 re-utilizations	58	0	58	0.15

S_{BET} = BET surface area.
V_{μ} = micropore volume by t-method.
S_{ext} = (mesopore + macropore) surface areas by t-method.
V_p = total pore volume.

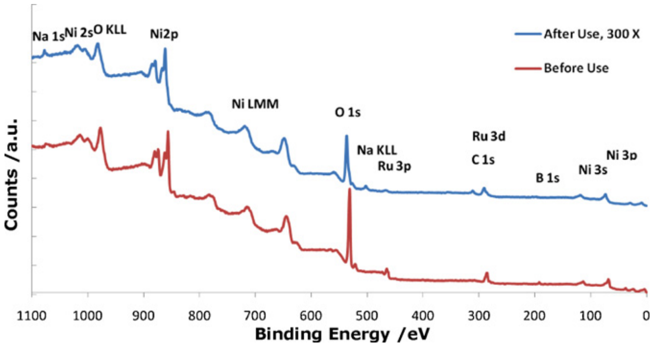

Fig. 9. Survey XPS spectra for the Ni–Ru based catalyst sample before and after 300 times re-used.

bond. The formation of borides, commonly referred in the literature [34], is not favored in this case, since aerated conditions and low temperature heat treatments were used. The apparent reduction in B content, after catalyst reused, might be associated to oxidation with the formation of boron oxides due to multiple annealing at 110 °C. Since the oxides are known to be water soluble, they are susceptible of being washed away during the conditioning of the catalyst implemented before repetitive use (see Section 2.).

Table 3 summarizes the XPS analysis results of the Ni–Ru based catalyst 300 times reused. The results showed that nickel (Ni 2p3) is the main metal surface constituent, 19.81 at.%. Ruthenium (Ru 3d5) contribution is about 1.42 at.%. Accordingly, the XPS data confirmed the increased in Ru concentration (Ru3d5) from 0.74 at.% (fresh sample) to 1.42 at. %. This almost twofold increased in Ru atomic concentration is thought to be due to segregation of ruthenium as a result of the intensive use in the catalyzed $NaBH_4$ hydrolysis.

3.2.2. *Variation in specific surface area of catalyst*

The Ni–Ru based catalyst, before and after reused 300 times, was also characterized by textural properties based on nitrogen adsorption isotherms.

Table 4 displays comparative data of catalyst total surface area and pore volume before and after 300 reutilizations. The values of surface areas, by BET and t-method, revealed 54 m^2/g and 58 m^2/g, respectively, before and after the ample use of the catalyst. As a result, an increased of 7.4% in the area is established, after 300 cycles, probably due to segregation of ruthenium. In fact, ruthenium segregation was confirmed by SEM and EDS. Ru-rich areas were found in the reused catalyst sample, as can be seen in Fig. 8. Therefore, it could be concluded that the continuous reuse of the Ni–Ru based catalyst, throughout the mentioned $NaBH_4$ hydrolysis schemes, enhanced some lost of Ru from the initial bimetallic alloy (Ni–Ru). And, due to the magnetic properties of these metals, the *vanished* Ru elements (from the bimetallic alloy) appear to agglomerate and form denser areas on the catalyst surface, which becomes richer in Ru element. Accordingly, the degradation of the studied catalyst seems to be caused by ruthenium segregation from the Ni–Ru alloy, which brought to diminishing the catalyst performance throughout its 300 long-life reutilizations.

4. Conclusions

In the present study, a powder nickel–ruthenium based catalyst long-life activity – all over 300 reutilizations – was checked by confronting the values of *yield*, *lag time* and *dP/dt* slopes (in the linear zone, of a graphical representation of hydrogen pressure inside the reactor as function of time), throughout two different schemes of $NaBH_4$ hydrolysis: *alkaline* and *alkali free* hydrolysis, performed in batch reactors with different internal volumes and bottom geometries (flat and conical). It was observed, for the *alkaline* $NaBH_4$ hydrolysis, that the H_2 generation rate progressively decreases with catalyst reused and only ~25% of the initial H_2 generation rate remains at 300 reutilizations. For similar periods of catalyst aging, it was observed that the reactor bottom geometry influences noticeably the H_2 generation rate regarding to the type of catalytic $NaBH_4$ hydrolysis: the conical bottom shape greatly enhances the H_2 generation rate (and practically eliminates the reaction induction time) in the solid or *alkali free* $NaBH_4$ hydrolysis. Consequently, the values obtained for the H_2 generation rates were among the most higher values found in the open literature.

To clarify the deterioration mechanism of the studied bimetallic catalyst, SEM, XPS and BET analysis have been made before and after 300× reutilizations. From SEM analysis, segregation of ruthenium from the Ni–Ru alloy surface catalyst was observed and EDS Ru-rich areas were found in the reused catalyst sample. Accordingly, the XPS data confirmed the increased in Ru concentration (Ru3d5) of almost twofold – from 0.74 at.% (fresh sample) to 1.42 at.% – which is thought to be due to segregation of ruthenium as a result of the intensive use in the catalyzed $NaBH_4$ hydrolysis. The values of surface areas, by BET and t-method, revealed an increased by 7.4% in the catalyst surface area, after 300 cycles. Consequently, the deterioration of the studied catalyst seems to be caused by ruthenium segregation from the Ni–Ru alloy, which brought to diminishing the catalyst performance throughout its 300 long-life reutilizations.

To conclude, the present work gives emphasis to the importance of considering both different schemes of $NaBH_4$ hydrolysis and the reactor bottom geometry in the study of catalyst durability. The two paths for H_2 generation from $NaBH_4$ hydrolysis, shown on the present manuscript, produced high H_2 pressure and can be generated in large amounts with enhanced energy densities, sufficient for use in PEMFC single cell and stack. Also, the capability of re-use a constant amount of catalyst during successive *refueling*, without any treatment and without significant loss of activity, is a major finding bearing in mind the possible applications of this concept for hydrogen generation and storage.

References

[1] V.A. Goltsov, T.N. Veziroglu, Int. J. Hydrogen Energy 26 (2001) 909–915.
[2] U.B. Demirci, P. Miele, Energy Environ. Sci. 2 (2009) 627–637.
[3] H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.E. Hoeskstra, K. Hyde, J. Am. Chem. Soc. 75 (1953) 215–219.
[4] E. Marrero-Alfonso, J.R. Gray, T.A. Davis, M.A. Matthews, Int. J. Hydrogen Energy 32 (2007) 4717–4722.
[5] U.B. Demirci, F. Garin, J. Alloy Compd. 463 (2008) 107–111.
[6] B.H. Liu, Z.P. Li, J. Power Sources 187 (2009) 527–534.
[7] U.B. Demirci, O. Akdim, J. Andrieux, J. Hannaver, R. Chamoun, P. Miele, Fuel Cells 10 (3) (2010) 335–350.
[8] U.S. Department of Energy Hydrogen Program. Available from: http://www.hydrogen.energy.gov/.
[9] J.H. Kim, K.T. Kim, Y.M. Kang, H.S. Kim, M.S. Song, J.Y. Lee, J. Alloy Compd. 379 (2004) 222–227.
[10] Q. Zhang, G. Smith, Y. Yu, R. Mohring, Int. J. Hydrogen Energy 31 (2006) 961–965.
[11] R. Peña-Alonso, A. Sicurelli, E. Callone, G. Carturan, R. Raj, J. Power Sources 165 (2007) 315–323.
[12] E. Keçeli, S. Özkar, J. Mol. Catal. A: Chem. 286 (2008) 87–91.
[13] P. Krishnan, S.G. Advani, A.K. Prasad, Int. J. Hydrogen Energy 33 (2008) 7095–7102.
[14] P. Krishnan, S.G. Advani, A.K. Prasad, Appl. Catal. B 86 (2009) 137.
[15] O.V. Komova, V.I. Simagina, O.V. Netskina, D.G. Kellerman, A.V. Ishchenco, N.A. Rudina, Catal. Today 138 (2008) 260–265.
[16] W. Ye, H. Zhang, D. Xu, L. Ma, B. Yi, J. Power Sources 164 (2007) 544–548.
[17] Y. Chen, H. Kim, Fuel Proc. Technol. 89 (2008) 966–972.
[18] U.B. Demirci, F. Garin, Catal. Commun. 9 (2008) 1167–1172.
[19] N. Patel, R. Fernandes, A. Miotello, J. Power Sources 188 (2009) 411–420.
[20] H.B. Dai, Y. Liang, P. Wang, X.D. Yao, T. Rufford, M. Lu, H.M. Cheng, Int. J. Hydrogen Energy 33 (2008) 4405–4412.
[21] K.-S. Eom, H.-S. Kwon, Int. J. Hydrogen Energy 35 (2010) 5220–5226.
[22] A.M.F.R. Pinto, D.S. Falcão, R.A. Silva, C.M. Rangel, Int. J. Hydrogen Energy 31 (2006) 1341–1347.
[23] M.J.F. Ferreira, V.R. Fernandes, C.M. Rangel, L. Gales, A.M.F.R. Pinto, J. N. Mater. Eletrochem. Syst. 12 (2009) 153–159.
[24] M.J.F. Ferreira, L. Gales, V.R. Fernandes, C.M. Rangel, A.M.F.R. Pinto, Int. J. Hydrogen Energy 35 (2010) 9869–9878.
[25] M.J.F. Ferreira, V.R. Fernandes, L. Gales, C.M. Rangel, A.M.F.R. Pinto, Int. J. Hydrogen Energy 35 (2010) 11456–11469.
[26] M.J.F. Ferreira, C.M. Rangel, A.M.F.R. Pinto, Hydrogen production by catalytic hydrolysis of sodium borohydride in batch reactors: new challenges, Int. J. Energy Research, under review.
[27] M.J.F. Ferreira, F. Coelho, C.M. Rangel, A.M.F.R. Pinto, Batch sodium borohydride hydrolysis systems: effect of sudden valve opening on hydrogen generation rate, Int. J. Hydrogen Energy, in press.
[28] 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.
[29] 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.
[30] P. Krishnan, T.-H. Yang, W.-Y. Lee, C.-S. Kim, J. Power Sources 143 (2005) 17–23.
[31] S. Özkar, M. Zahmakiran, J. Alloy Compd. 404–406 (2005) 728–731.
[32] S.U. Jeong, R.K. Kim, E.A. Cho, H.-J. Kim, S.-W. Nam, I.-H. Oh, J. Power Sources 144 (2005) 129–134.
[33] J. Zhang, Y. Zheng, J.P. Gore, T.S. Fisher, J. Power Sources 165 (2007) 844–853.
[34] D. Hua, Y. Hanxi, A. Xinping, C. Chuansin, Int. J. Hydrogen Energy 28 (2003) 1095–1100.
[35] Y. Kojima, Y. Kawai, H. Nakanishi, S. Matsumoto, J. Power Sources 35 (2004) 36–41.
[36] U.B. Demirci, O. Akdim, P. Miele, Int. J. Hydrogen Energy 34 (2009) 2638–2645.