A direct measurement of the heat evolved during the sodium and potassium borohydride catalytic hydrolysis

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ABSTRACT

$NaBH_4$ and KBH_4 hydrolysis reactions ($BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2$), which can be utilized as a source of high purity hydrogen and be easily controlled catalytically, are exothermic processes. Precise determination of the evolved heat is of outmost importance for the design of the reactor for hydrogen generation. In this work we present an efficient calorimetric method for the direct measurement of the heats evolved during the catalyzed hydrolysis reaction. A modified Setaram Titrys microcalorimeter was used to determine the heat of hydrolysis in a system where water is added to pure solid $NaBH_4$ or KBH_4 as well as to solid $NaBH_4$ or KBH_4 mixed with a Co-based solid catalyst. The measured heats of $NaBH_4$ hydrolysis reaction were: $-236\,kJ\,mol^{-1}$, $-243\,kJ\,mol^{-1}$, $-235\,kJ\,mol^{-1}$, and $-236\,kJ\,mol^{-1}$, without catalyst and in the presence of Co nanoparticles, CoO and Co_3O_4, respectively. In the case of the KBH_4 hydrolysis reaction, the measured heats were: $-220\,kJ\,mol^{-1}$, $-219\,kJ\,mol^{-1}$, $-230\,kJ\,mol^{-1}$, and $-228\,kJ\,mol^{-1}$, without catalyst and with Co nanoparticles, CoO and Co_3O_4, respectively. Also, a comparison was made with an aqueous solution of $CoCl_2 \cdot 6H_2O$ used as catalyst in which case the measured heats were $-222\,kJ\,mol^{-1}$ and $-196\,kJ\,mol^{-1}$ for $NaBH_4$ and KBH_4 hydrolysis, respectively. The influence of solid NaOH or KOH additions on the heat of borohydride hydrolysis has been investigated as well.

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1. Introduction

Interest in hydrogen as a fuel to satisfy the growing demand for efficient and clean energy has increased significantly during the past decade and many improvements have been accomplished. When compared to common fossil fuels such as coal, petrol and natural gas, hydrogen, as a combustible fuel, exhibits the highest heating value per kg (12.24×10^4 kJ) [1]. Also hydrogen is environmentally friendly. However the development of appropriate hydrogen storage technologies still represents a challenge due to the low volumetric density of hydrogen.

Sodium and potassium borohydrides ($NaBH_4$ and KBH_4) are recognized as excellent materials for hydrogen storage [2]. These compounds have a good gravimetric storage capacity and their alkaline solutions are safe for transportation. They can be utilized as sources of high purity hydrogen generated by the hydrolysis reaction, Eq. (1), which is easy to control catalytically [3]:

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2 \qquad (1)$$
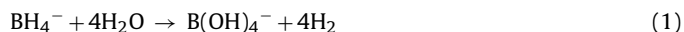
Half of the hydrogen produced originates from the water, as shown in Eq. (1), which is also an advantage of this reaction. In the case of $NaBH_4$ hydrolysis, the by-product sodium metaborate ($NaBO_2$), is not a pollutant so it can be safely discarded without further treatment (it is commonly found in laundry detergents), and it can be recycled as the starting material for the synthesis of $NaBH_4$ [4].

The minimum value for hydrogen storage capacity recommended by the U.S. Department of Energy is 6.5 wt% [5]. $NaBH_4$ has a high hydrogen content, 10.8 wt%, while KBH_4 contains 8.9 wt% of hydrogen, when the weight of water is taken into account. It is important to note that the hydrogen storage capacity of borohydrides depends on the quantity of water involved [6]. These compounds can find applications in mobile and portable fuel cell systems, since they produce the pure and slightly humid hydrogen necessary for polymer electrolyte membrane (PEM) cells. It has been shown that sodium borohydride can be used directly in a PEM fuel cell and it can achieve high system energy densities [7].

Hydrolysis of $NaBH_4$ and KBH_4 is a very slow process and the rate of hydrogen generation from this reaction depends on the catalyst used and its preparation method [8]. The use of a suitable catalyst allows the hydrogen generation rate to be controlled on demand, thereby avoiding the safety risks involved in high-pressure H_2 delivery systems.

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Numerous catalysts have been investigated to accelerate the hydrogen generation rate in hydrolysis of borohydrides. While noble metal catalysts show excellent catalytic activity, their use in practical applications is restricted by their high cost and availability. Low cost transition metal catalysts with high performance are attractive for the development of on-board systems for hydrogen generation by catalytic hydrolysis of borohydrides. Particularly, catalytic materials based on Co have shown high activity and stability for the hydrolysis reaction and there have been many reports in the literature about activities of various Co-based catalysts: Raney Ni–Co alloys [9], cobalt on different supports [10–14,], Co_3O_4 and $LiCoO_2$ [15], $CoCl_2$ [16], $Pt-LiCoO_2$ [17], etc.

Hydrolysis of $NaBH_4$ and KBH_4 is an exothermic process, and the measurement of the heat evolved during the catalytic reaction is important from both the practical (thermal risk assessment) and fundamental (thermodynamic data for the determination of the reaction mechanism) points of view. The reactor temperature increases during the hydrolysis of borohydrides, which may result in a sharp pressure increase. This temperature and pressure increase should be concerned when handling borohydrides and constructing reactors for hydrogen generation. Hence, precise measurement of the heat of reaction is of great importance for system design and feasibility studies.

The reaction of $NaBH_4$ hydrolysis has been extensively studied and the obtained results have been recently reviewed [18,19], while the number of papers concerning KBH_4 hydrolysis is very limited [20–22]. Moreover, values for the theoretical, calculated energy of borohydride hydrolysis reaction are inconsistent and actual experimental data are surprisingly rare [6].

Calorimetric techniques, and liquid-phase calorimetry in particular, are promising methods to study catalytic reactions [23]. In this work we present an efficient calorimetric method for the direct measurement of the heats evolved during $NaBH_4$ and KBH_4 hydrolysis in the presence of several Co-based catalysts, providing information about reaction thermodynamics and kinetics. The cobalt-based compounds used in this work are commercially produced in large quantities and represent cheap and attractive sources for applications as catalysts for hydrogen generation.

2. Experimental

In this work the following chemicals were used: $NaBH_4$ (Strem Chemicals, 93-1118), KBH_4 (Aldrich, 455571-100G), NaOH (Aldrich, 655104-500G), KOH (Sigma–Aldrich, 306568-100G), Co nanoparticles (Strem Chemicals, 270020), $CoCl_2·6H_2O$ (Strem Chemicals, 93-2734), CoB (Aldrich, 33677-7-5G), CoO (Aldrich, 52944-3-5G) and Co_3O_4 (Strem Chemicals, 27-0490). Prior to the experiments, all the chemicals were stored, handled and prepared in an argon-purged glove box.

Distilled water saturated with N_2 was used in all experiments. Each test was repeated three times in order to verify reproducibility. $NaBH_4$ as well as KBH_4 was heated at 150 °C for 12 h under vacuum before measurements.

Titration microcalorimetry. A specially modified Setaram Titrys microcalorimeter was used to determine the heat of hydrolysis in a system where water excess ($H_2O/NaBH_4 = 70$ mol mol^{-1} and $H_2O/KBH_4 = 100$ mol mol^{-1}) was added to pure solid $NaBH_4$ or KBH_4 as well as to solid $NaBH_4$ or KBH_4 mixed with catalyst. The instrument used was a Calvet type differential heat flow microcalorimeter which allows continuous stirring of liquid–solid mixtures [24,25]. The experiments were performed at 303 K. In each experiment, 30 mg of dry $NaBH_4$ or KBH_4 powder and an appropriate amount of solid catalyst, equivalent to 10 wt% of pure Co with respect to sodium or potassium borohydride, were placed in the sample cell under Ar atmosphere. For the experiments including
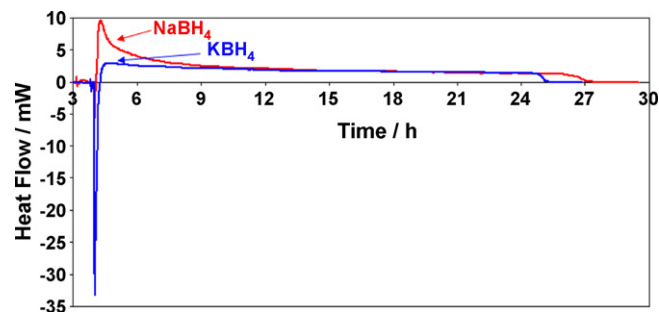

Fig. 1. Heat flow signals versus time for $NaBH_4$ and KBH_4 hydrolysis without catalyst.

NaOH or KOH, 5.5 mg of the hydroxide was mixed together with $NaBH_4$ or KBH_4 and the catalyst powder. The sealed cell was then transferred from the glove box to the calorimeter. After stabilization of the calorimeter baseline, 1 ml of water was added (rate of injection 3 ml min^{-1}) to the sample cell and to the empty reference cell in the same way using a programmable twin syringe pump PHD 2000, from Harvard Apparatus, linked to the calorimeter by capillary tubes. When $CoCl_2·6H_2O$ was used as a catalyst, 1 ml of aqueous 0.05 M solution of $CoCl_2·6H_2O$ was injected in the sample cell (rate of injection 3 ml min^{-1}) which contained the same amounts of dry borohydrides and hydroxides as in other performed experiments. The amount of $CoCl_2·6H_2O$ used was equivalent to 10 wt% of pure Co with respect to sodium or potassium borohydride, as in the case of other investigated catalysts. The reaction cell had a home-made air-tight cap with attached inox outlet tube. The inox tube was linked to a gas volume meter from Ritter allowing continuous measurement of generated hydrogen.

3. Results and discussion

3.1. Hydrolysis reactions of $NaBH_4$ and KBH_4 without catalyst

The rate of borohydride hydrolysis reaction without catalyst is very low. Fig. 1 shows the heat flow evolved during the hydrolysis reactions of $NaBH_4$ and KBH_4 without catalyst. The endothermic signal visible on the heat flow versus time curves for both investigated borohydrides coincides with the water injection. The hydrolysis reaction is an exothermic process and, after an initial increase, the heat flow signal reaches an almost constant value until the end of hydrolysis reaction, when it exhibits an abrupt decrease.

$NaBH_4$ is more soluble in water than KBH_4 (55 g/100 g H_2O for $NaBH_4$ and 19 g/100 g H_2O for KBH_4 at 25 °C [22]), hence the endothermic signal originating from dissolution of borohydrides is smaller in the case of $NaBH_4$. The areas of the endothermic peaks correspond to values of about +6 kJ mol^{-1} for $NaBH_4$ and +12 kJ mol^{-1} for KBH_4. Since the energy of $NaBH_4$ dissolution in water is +32.2 kJ mol^{-1} [26], this negative heat flow (endothermic) signal also includes a contribution of an exothermic signal originating from the hydrolysis reaction which starts immediately after water injection and which is difficult to separate experimentally; the values obtained by integration of the endothermic peaks are within the experimental error.

Under experimental conditions where a large excess of water was added to anhydrous $NaBH_4$ or KBH_4 at 303 K, it took more than 1 day for the reaction to be completed. Long time scale experiments are challenging in terms of accuracy of the total evolved heat (integral method) determination. In order to overcome this problem each experiment was repeated three times. The average measured heats for the hydrolysis reaction without catalyst were −236 kJ mol$^{-1}_{NaBH_4}$ and −220 kJ mol$^{-1}_{KBH_4}$ (±3 kJ mol^{-1}).

The value of the measured heat includes the enthalpy of dissolution of the borohydride, the enthalpy of the hydrolysis reaction, the enthalpy of dissolution of the by-product ($NaBO_2$ or KBO_2) and the evaporation of water during the exothermic reaction.

In the case of $NaBH_4$, taking into account the energy of $+32\,kJ\,mol^{-1}_{NaBH_4}$ consumed to dissociate $NaBH_4$ into Na^+ and BH_4^- [26] and the loss of water vapor at 303 K with an estimated energy of $7.4\,kJ\,mol^{-1}_{NaBH_4}$ [27], the calorimetric measurement of a total energy of $-236\,kJ\,mol^{-1}_{NaBH_4}$ corresponds to an experimentally determined hydrolysis enthalpy of about $-275\,kJ\,mol^{-1}_{NaBH_4}$.

Theoretically, increasing the water content can lead to following reaction [19]:

$$NaBH_4 + 6H_2O \rightarrow NaBO_2 \cdot 4H_2O + 4H_2 \qquad (2)$$
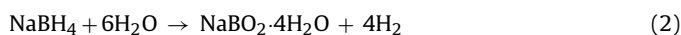
Since our experiments were performed in the presence of a large excess of water, Eq. (2) is applicable to our results. Using Eq. (2) the standard-state enthalpy change for $NaBH_4$ hydrolysis can be calculated from standard formation enthalpies at 25 °C: $-188.6\,kJ\,mol^{-1}$ ($NaBH_4$) [28], $-285.8\,kJ\,mol^{-1}$ (H_2O) [28], $-2175.7\,kJ\,mol^{-1}$ ($NaBO_2\cdot4H_2O$) [29], resulting in $\Delta_r H^0 = -272.1\,kJ\,mol^{-1}_{NaBH_4}$, which is in very good agreement with the value obtained in this study.

The analogous calculation for the KBH_4 hydrolysis reaction is impossible since, to the best of our knowledge, the necessary experimentally determined thermodynamic properties of potassium borohydride and potassium metaborates are not available in the literature. Moreover, our aim was more to obtain real heats evolved during hydrolysis reactions necessary for actual application in portable devices.

3.2. Hydrolysis reaction of $NaBH_4$ and KBH_4 in the presence of Co-based solid catalysts

Heterogeneous catalysts have the advantage of easy separation from the hydrolyzed solution. Compared to homogeneous acid catalysts, these catalysts are easily recycled [30]. Particularly, Co-based catalyst, due to magnetic properties of Co, can be easily separated with permanent magnets and reused [31]. Moreover, homogeneous catalysts for borohydride hydrolysis are considered good for continuous hydrogen production, but not suitable for on demand hydrogen production because of the difficulty to stop the reaction process [19].

3.3. $NaBH_4$ hydrolysis

The catalytic hydrolysis of $NaBH_4$ and KBH_4 is a complex process which involves solid-phase dissolution and liquid-phase transfer of the reactant and by-product, while the reaction occurs at the catalyst surface. The Co-based catalysts studied in this work were commercially available compounds: Co nanoparticles, CoO, Co_3O_4 and CoB. Fig. 2 shows the heat flow evolution versus time during $NaBH_4$ hydrolysis reaction in the presence of different Co-based catalysts.

The measured heats of the $NaBH_4$ hydrolysis reaction were $-243\,kJ\,mol^{-1}_{NaBH_4}$, $-235\,kJ\,mol^{-1}_{NaBH_4}$, and $-236\,kJ\,mol^{-1}_{NaBH_4}$ for Co nanoparticles, CoO, and Co_3O_4, respectively. The sharp decrease of each heat flow signal corresponds to the end of hydrogen generation. Tests were also performed with CoB, but under the given experimental conditions this compound did not increase the rate of hydrolysis reaction, i.e. it did not show any catalytic activity. Indeed, the particle size of commercial CoB tested in this study, covered with a thick layer of oxide prevented this compound from being active.

Obtained results from calorimetric measurements, performed in nitrogen atmosphere, allow us to conclude that the same active
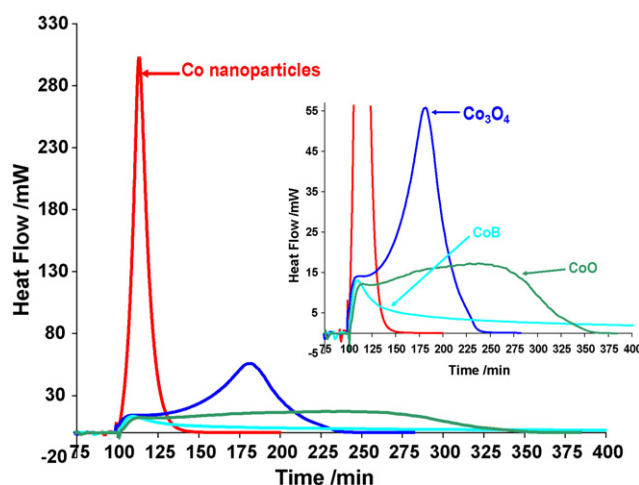

Fig. 2. Heat flow signals versus time for $NaBH_4$ hydrolysis reaction in the presence of different Co-based solids.

phase is formed *in situ* in the case of Co nanoparticles, Co_3O_4 and CoO. When stirring was stopped and calorimetric cell opened, black precipitate was present in the reaction cell after every experiment with Co-based catalysts. It is known, that cobalt boride species formed *in situ* by chemical reduction of Co^{2+} or Co^{3+} with sodium borohydride are the active phase for hydrolysis of $NaBH_4$ in the presence of cobalt-based catalysts [6,10,13,15,23]. Formation of catalytically active phase, prior to hydrolysis reaction, strongly depends on reaction conditions. When the reaction is performed under anaerobic conditions, reduction of Co^{2+} with $NaBH_4$ in aqueous solution yields black Co_2B as the primary product, while exposure to air results in conversion of cobalt boride into metallic Co and boron oxides [32].

It has been reported that, in the presence of $NaBH_4$, Co nanoparticles [23] and Co_3O_4 [15] are reduced to form catalytically active cobalt boride. The rapid increase of the heat flow signal after an initial delay indicates the time required to form cobalt boride from Co_3O_4. A delayed start is recorded in the case of CoO as well, also due to the formation of active phase in the reaction medium, but the evolution of heat is different from that observed with Co_3O_4 and remains almost constant during the hydrolysis reaction. The catalytically active phase formed from Co_3O_4 showed higher activity than that formed from CoO. Moreover, a slow hydrolysis reaction can lead to more side products, thus decreasing the amount of active phase formed [15]. In the case of Co nanoparticles, the particles are known [23] to have a very homogeneous size distribution (average diameter 10–12 nm) and to be covered by an oxide layer which needs to be reduced prior to the *in situ* formation of active phase. However, both the heat flow evolution and the hydrogen volume generation suggest that these processes are happening significantly faster than the formation of active phase from Co_3O_4 and CoO.

The reaction times for hydrogen generation were: 33 min for Co nanoparticles, 120 min for Co_3O_4, 240 min for CoO and over 24 h for commercial CoB (the same as without catalyst). In all cases, 100% of the stoichiometric amount of hydrogen is generated during the stated reaction time. The volume of hydrogen generated by $NaBH_4$ hydrolysis in the presence of Co nanoparticles, CoO and Co_3O_4 is plotted versus time in Fig. 3. In the presence of CoB the rate of the hydrolysis reaction was too slow to enable monitoring of the kinetics.

The rate of the $NaBH_4$ hydrolysis reaction versus time in the presence of Co nanoparticles, CoO and Co_3O_4 is shown in Fig. 4. For Co nanoparticles and Co_3O_4, the rate increases to reach a maximum value and then decreases after approximately 50% of the conversion
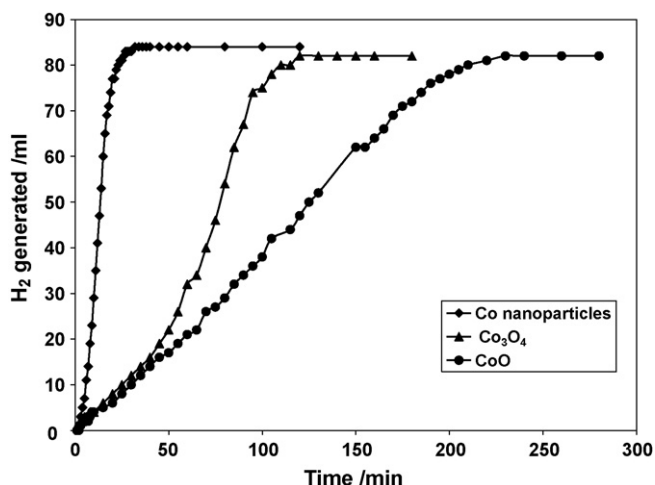
Fig. 3. Evolution versus time of the hydrogen generation for $NaBH_4$ hydrolysis in the presence of Co nanoparticles, CoO and Co_3O_4.

has been achieved due to a decrease in $NaBH_4$ concentration. The maximum rates reached with Co nanoparticles and Co_3O_4 were $6\,ml\,min^{-1}$ and $1.6\,ml\,min^{-1}$ respectively, i.e. $2\,l\,min^{-1}\,g^{-1}$ of Co and $0.53\,l\,min^{-1}\,g^{-1}$ of Co. The rate of the reaction with CoO was constant with time, at $0.4\,ml\,min^{-1}\,g^{-1}$, i.e. $0.13\,l\,min^{-1}\,g^{-1}$ of Co.

It is clear from the presented results that Co nanoparticles show the best catalytic performance for $NaBH_4$ hydrolysis reaction compared to the other investigated Co-based catalysts, accompanied with the highest amount of evolved heat. Also, a similarity can be observed in the profiles shown in Fig. 4 with the heat calorimetric curves plotted in Fig. 2.

3.3.1. KBH_4 hydrolysis

The same Co-based catalysts have been used for the determination of heat evolved during the catalytic hydrolysis reaction of KBH_4. It is considered that KBH_4 is not a suitable hydrogen storage material due to its low gravimetric density of hydrogen, slow kinetics and high production cost compared to $NaBH_4$ [19]. However, KBH_4 has better hygroscopic properties than $NaBH_4$ [22] and releases less heat during hydrolysis reaction, which might be of importance for potential reactor design.

The experimental calorimetric curves obtained for the hydrolysis reaction of KBH_4 in the presence of Co nanoparticles, CoO, Co_3O_4 and CoB, are shown in Fig. 5.

The measured heats of the KBH_4 hydrolysis reaction were $-219\,kJ\,mol^{-1}$, $-230\,kJ\,mol^{-1}$ and $-228\,kJ\,mol^{-1}$ in the presence
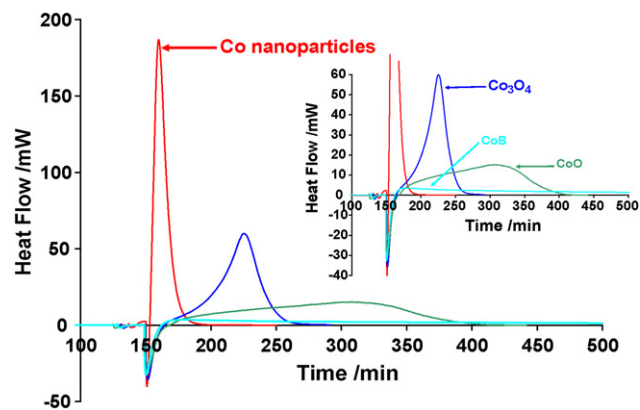
of Co nanoparticles, CoO and Co_3O_4, respectively. As in the case of $NaBH_4$ hydrolysis, CoB did not show any catalytic influence on the rate of reaction. The shapes of the curves are similar for $NaBH_4$ and KBH_4, but less heat is generated during the KBH_4 hydrolysis reaction. A delay in the start of the hydrolysis reaction is detected in the cases of Co_3O_4 and CoO due to the formation of catalytically active phase, similarly to what was observed for $NaBH_4$ hydrolysis. Also, in the case of KBH_4 hydrolysis an endothermic peak remains present just after the water injection, as in the experiment without catalyst. Since the solubility of KBH_4 in water is smaller than that of $NaBH_4$, even though in the presence of catalyst the hydrolysis reaction rate is significantly increased, the contribution of the endothermic signal is higher for KBH_4 than for $NaBH_4$, but the integrated value of this signal is negligible compared to the total evolved heat.

Fig. 6 shows the volume of hydrogen generated versus time for KBH_4 hydrolysis in the presence of Co nanoparticles, CoO and Co_3O_4.

The rate of the reaction with CoB was too slow to be followed. However, 100% of conversion was obtained after 20 min with Co nanoparticles, 100 min with Co_3O_4 and 210 min with CoO.

The rate of the KBH_4 hydrolysis reaction in the presence of Co nanoparticles, CoO and Co_3O_4 is shown in Fig. 7. For Co nanoparticles and Co_3O_4, the rate increases to a maximum and then decreases. The rates achieved for Co nanoparticles and Co_3O_4 were respectively $6\,ml\,min^{-1}$ and $1.5\,ml\,min^{-1}$, i.e. $2\,l\,min^{-1}\,g^{-1}$ of Co and $0.5\,l\,min^{-1}\,g^{-1}$ of Co. For CoO, the rate was constant and was about $0.4\,ml\,min^{-1}$, i.e. $0.13\,l\,min^{-1}\,g^{-1}$ of Co.

The H_2 generation rates obtained for KBH_4 hydrolysis in the presence of Co nanoparticles, CoO and Co_3O_4 are the same as for

Fig. 5. Heat flow signals versus time for KBH_4 hydrolysis reaction in the presence of different Co-based solids.

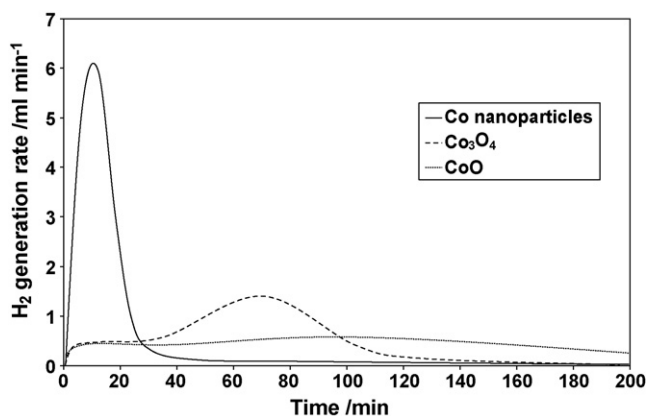

Fig. 4. The rate of the $NaBH_4$ hydrolysis reaction versus time in the presence of Co nanoparticles, CoO and Co_3O_4.
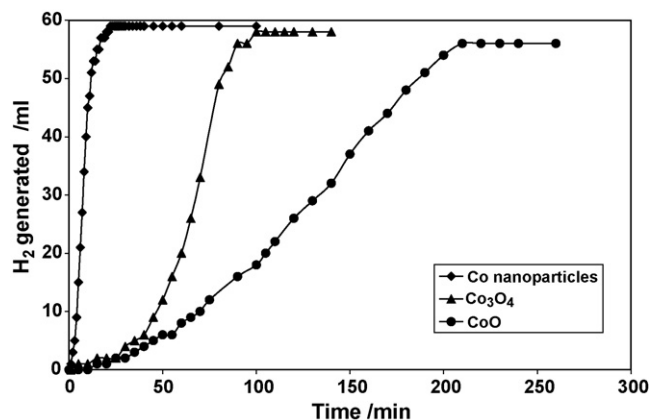

Fig. 6. Evolution versus time of the hydrogen generation for KBH_4 hydrolysis in the presence of Co nanoparticles, CoO and Co_3O_4.

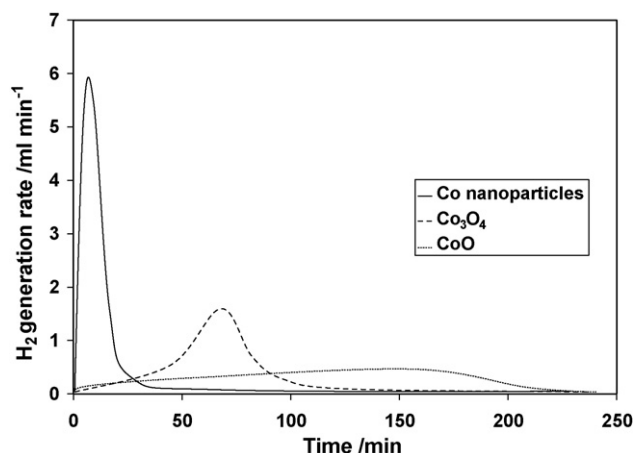**Fig. 7.** The rate of the KBH_4 hydrolysis reaction versus time in the presence of Co nanoparticles, CoO and Co_3O_4.

Fig. 8. Heat flow signals versus time for $NaBH_4$ hydrolysis reaction in the presence of different Co-based solids and 0.5 wt% of NaOH.

$NaBH_4$ hydrolysis, but the volume of generated hydrogen is smaller due to the lower storage capacity of KBH_4.

3.4. Influence of hydroxide addition

It is well known that $NaBH_4$ is quite stable when maintained at high pH. Base-stabilized $NaBH_4$ solution will not hydrolyze without the presence of a catalyst. NaOH is predominantly used for the stabilization of $NaBH_4$ aqueous solutions, as it is more available and affordable compared to other hydroxides. It has been shown that alkali addition has an influence on $NaBO_2$ solubility: it differs greatly depending on the alkali hydroxide used, but the addition of 1 wt% of NaOH or KOH results in a minor solubility improvement compared to the solution containing no hydroxide [4]. KOH is shown to be a better alkali additive to maintain the hydrolysis by-products in solution, since the effective radius of K^+ is larger than that of Na^+, thus having smaller hydration shell and leaving more H_2O available [4]. While more than 1 wt% of NaOH results in solute precipitation, 10 wt% of KOH is considered to be the optimal concentration under which the interference of $NaBO_2$ precipitate with H_2 generation will be minimized [4].

In this work we used 0.5 wt% of NaOH and KOH in order to investigate the influence of these additives on the calorimetric effects and the rate of hydrogen generation of $NaBH_4$ and KBH_4 hydrolysis while preserving a maximum solubility of the by-products.

3.4.1. NaBH4 hydrolysis in the presence of NaOH

The same experiments ($NaBH_4$ hydrolysis in the presence of the investigated Co-based catalysts) have been performed with an addition of NaOH.

Fig. 8 shows the heat flow evolution versus time during the $NaBH_4$ hydrolysis reaction in the presence of the investigated catalysts and 0.5 wt% of NaOH.

The measured heats of reaction were $-240 \, kJ \, mol^{-1}$, $-237 \, kJ \, mol^{-1}$ and $-232 \, kJ \, mol^{-1}$ for Co nanoparticles, Co_3O_4 and CoO, respectively. In the case of Co nanoparticles and Co_3O_4 the reaction rate was enhanced by the addition of NaOH, while no changes were detected for CoO. Concerning the investigated solid which did not show any catalytic activity for $NaBH_4$ hydrolysis (CoB), the addition of NaOH had no influence on the rate of reaction when CoB was used as a catalyst.

The heat of dissolution of NaOH was negligible, so the warming effect was insufficient to influence catalytic activity. Indeed, the energy of dissolution is $-44 \, kJ \, mol^{-1}$ [28], so the dissolution of 5.5 mg of NaOH in water will result in only 6 J. On the other hand, the reduction mechanism through which the active phase is formed
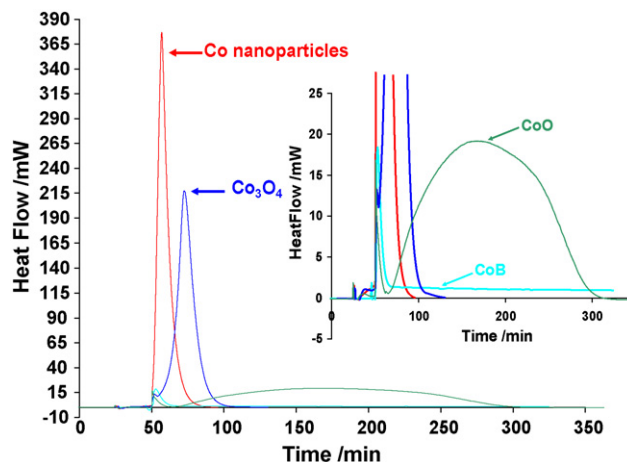
is known to be faster at high pH [33]; a higher level of Co^{2+} reduction results in a higher amount of active phase, and hence a higher activity. Also, the hydrolysis reaction rate increases linearly with increasing $[OH^-]$ [16], resulting in a higher H_2 generation rate.

Fig. 9 shows the volume of hydrogen generated versus time for $NaBH_4$ hydrolysis in the presence of Co nanoparticles, CoO, Co_3O_4 and CoB. The rate of hydrogen generation increased with addition of NaOH in the case of Co nanoparticles, Co_3O_4 (see Fig. 3), while no changes were detected in the case of CoO and CoB.

It took 20 min, 35 min and 240 min to obtain 100% of conversion over Co nanoparticles, Co_3O_4 and CoO, respectively.

Fig. 10 presents the rate of the $NaBH_4$ hydrolysis reaction versus time in the presence of Co nanoparticles, CoO or Co_3O_4 and 0.5 wt% of NaOH. The maximum rates reached over Co nanoparticles and Co_3O_4 were $13 \, ml \, min^{-1}$ and $8 \, ml \, min^{-1}$ respectively, i.e. $4.3 \, l \, min^{-1} \, g^{-1}$ of Co and $2.6 \, l \, min^{-1} \, g^{-1}$ of Co. For CoO, the reaction rate was constant over time at $0.4 \, ml \, min^{-1}$, i.e. $0.13 \, l \, min^{-1} \, g^{-1}$ of Co, the same as without NaOH.

3.4.2. KBH4 hydrolysis in the presence of NaOH or KOH

Since Co nanoparticles and Co_3O_4 have shown the highest activities as catalysts for borohydride hydrolysis compared to the other Co-based catalysts investigated in this work, these two solids were selected for an investigation of the influence of addition of NaOH and KOH on the heat evolved during hydrolysis reaction.
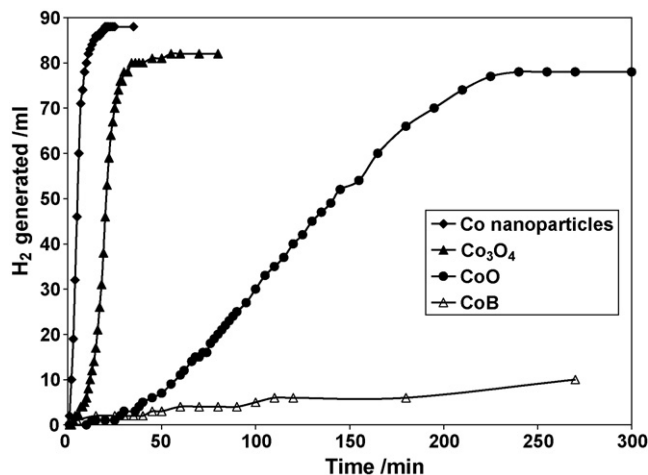

Fig. 9. Evolution versus time of the hydrogen generation for $NaBH_4$ hydrolysis in the presence of Co nanoparticles, CoO, Co_3O_4 or CoB and 0.5 wt% of NaOH.
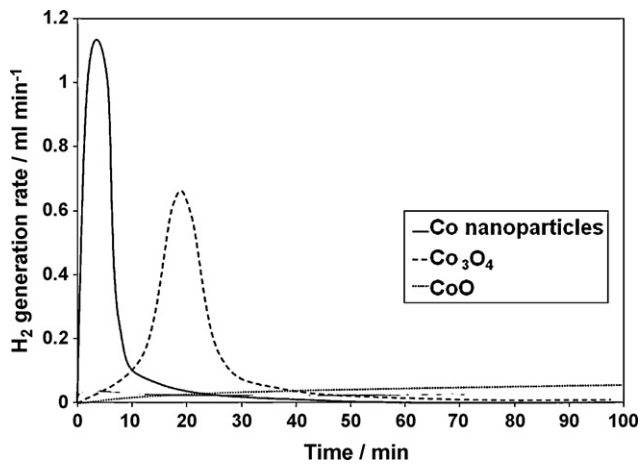
Fig. 10. The rate of the $NaBH_4$ hydrolysis reaction versus time in the presence of Co nanoparticles, CoO or Co_3O_4 and 0.5 wt% of NaOH.

Fig. 11(a) shows the experimental calorimetric curves obtained for the hydrolysis of KBH_4 in the presence of Co nanoparticles and 0.5 wt% of hydroxides (NaOH or KOH). The measured heats were $-226\,kJ\,mol_{KBH_4}^{-1}$ and $-220\,kJ\,mol_{KBH_4}^{-1}$ in the presence of 0.5 wt% of NaOH and 0.5 wt% of KOH, respectively. The evolved heats in

both experiments were the same within the experimental error, as well as the reaction times; 100% conversion was accomplished after 15 min in both experiments (see Fig. 11(b)). The hydrolysis reaction rate increased in the presence of hydroxides, but not significantly, and no influence of the nature of the hydroxide on the rate of reaction could be detected.

The heat flow evolved during the KBH_4 hydrolysis reaction and the volume of generated H_2 versus time in the presence of Co_3O_4 and 0.5 wt% of NaOH and 0.5 wt% of KOH are shown in Fig. 12.

The measured heats of KBH_4 hydrolysis reaction catalyzed by Co_3O_4 in the presence of 0.5 wt% of NaOH and 0.5 wt% of KOH were $-240\,kJ\,mol^{-1}$ and $-226\,kJ\,mol^{-1}$, respectively. The reaction times were 40 min and 60 min for 0.5 wt% of NaOH and 0.5 wt% of KOH, respectively. The KBH_4 hydrolysis reaction was enhanced in the presence of both hydroxides, but the increase of the reaction rate was more pronounced in the case of NaOH. When the same weight percentage of NaOH and KOH is present in the same volume of reaction mixture, molarity of KOH is smaller than molarity NaOH. Since the hydrolysis reaction rate increases linearly with $[OH^-]$ concentration [16], a more pronounced increase in the reaction rate in the case of NaOH is justified.

This effect was not detected in the case of Co nanoparticles, most probably because of the smaller particle size which resulted in the faster formation of catalytically active phase.
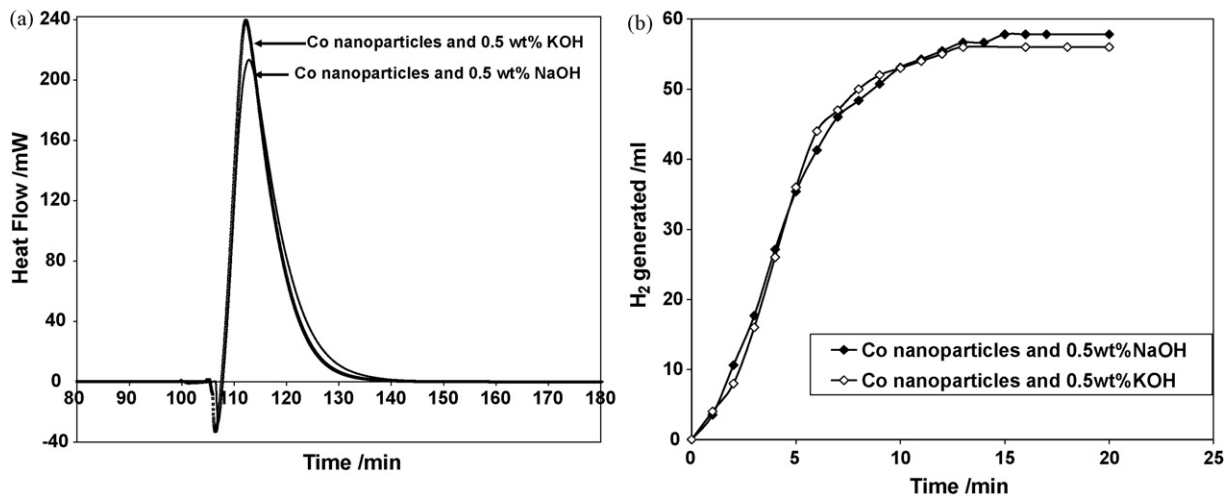

Fig. 11. KBH_4 hydrolysis reaction in the presence of Co nanoparticles and 0.5 wt% of NaOH or 0.5 wt% of KOH: (a) heat flow signals versus time; (b) evolution versus time of the hydrogen generation.
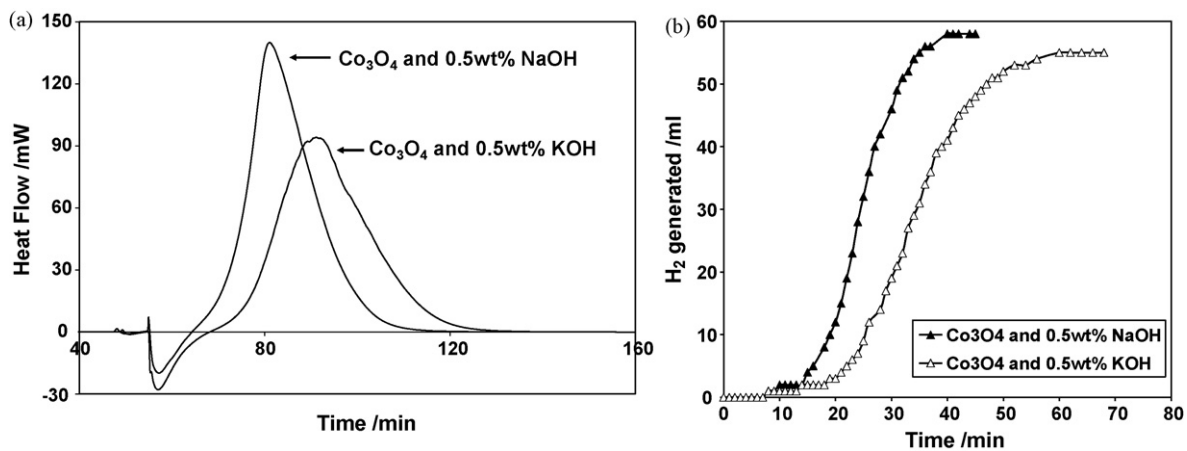

Fig. 12. KBH_4 hydrolysis reaction in the presence of Co_3O_4 and 0.5 wt% of NaOH or 0.5 wt% of KOH: (a) heat flow signals versus time; (b) evolution versus time of the hydrogen generation.
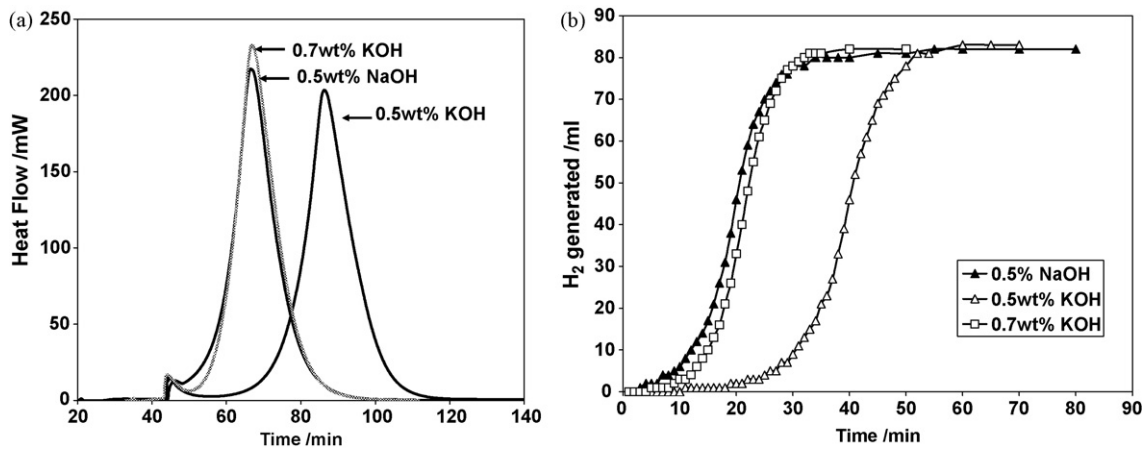
Fig. 13. $NaBH_4$ hydrolysis reaction in the presence of Co_3O_4 and 0.5 wt% of NaOH or 0.5 wt% or 0.7 wt% of KOH: (a) heat flow signals versus time; (b) evolution versus time of the hydrogen generation.

3.4.3. Influence of the hydroxide on the hydrolysis of $NaBH_4$

Completely analogous results have been obtained for the $NaBH_4$ hydrolysis reaction catalyzed by Co nanoparticles or Co_3O_4 in the presence of the same weight percentages (0.5 wt%) of NaOH or KOH. The presence of hydroxides increased the reaction rates for both catalysts used. However, while the increases in reaction rate were the same for NaOH and KOH when Co nanoparticles were used, in the presence of Co_3O_4 the addition of NaOH resulted in a higher enhancement of the $NaBH_4$ hydrolysis rate than the same mass of KOH. Correspondingly, hydrogen generation by $NaBH_4$ hydrolysis catalyzed by Co_3O_4 was faster in the presence of 0.5 wt% of NaOH than with 0.5 wt% KOH, as shown in Fig. 13(b).

In order to investigate the influence of the hydroxide cations, we have performed experiments using the same molar amounts of NaOH or KOH in the presence of Co_3O_4. Fig. 13(a) shows the experimental calorimetric curves obtained for the hydrolysis reaction of $NaBH_4$ in the presence of Co_3O_4 and 0.5 wt% of NaOH, 0.5 wt% of KOH, or 0.7 wt% of KOH which is the molar amount equivalent to 0.5 wt% of NaOH used in the experiments.

The measured heats were $-237 \, kJ \, mol^{-1}_{NaBH_4}$, $-242 \, kJ \, mol^{-1}_{NaBH_4}$ and $-240 \, kJ \, mol^{-1}_{NaBH_4}$ in the presence of 0.5 wt% of NaOH, 0.5 wt% of KOH and 0.7 wt% of KOH, respectively. Full conversion was achieved after 35 min, 60 min and 35 min for 0.5 wt% of NaOH, 0.5 wt% of KOH and 0.7 wt% of KOH, respectively. It is obvious from these results that the same molar amounts of NaOH and KOH have exactly the same influence on the hydrolysis reaction rate when Co_3O_4 is used as a catalyst. It can be concluded that at equal water/alkali molar

ratios, i.e. at equal pH of solutions, the rate of the hydrolysis of BH_4^- ions is independent of the nature of the alkali metal cations (Na^+ and K^+). This finding is in agreement with results obtained for sodium borohydride hydrolysis which can be found in the literature [22,34].

3.5. Hydrolysis of $NaBH_4$ and KBH_4 in the presence of $CoCl_2$ aqueous solution

In order to obtain an active catalyst finely distributed in the reaction mixture, we have studied the addition of cobalt chloride aqueous solution on the solid borohydrides. It is known that the catalytic mechanism for borohydride hydrolysis over $CoCl_2 \cdot 6H_2O$ is first an acidic reaction, i.e. the direct reaction of borohydride with acid in parallel with *in situ* formation of a cobalt boride phase, and then subsequent catalysis [3]. This reaction is fast with abrupt increase of temperature due to the heat evolved which can raise safety concerns in potential applications.

Fig. 14(a) shows the experimental calorimetric curves obtained for the hydrolysis reaction of $NaBH_4$ and KBH_4 in the presence of cobalt chloride solution. The measured heats of the hydrolysis reaction were $-222 \, kJ \, mol^{-1}_{NaBH_4}$ and $-196 \, kJ \, mol^{-1}_{KBH_4}$. 100% conversion was achieved after 10 min and 8 min for $NaBH_4$ and KBH_4, respectively. The volume of hydrogen generated is presented as a function of time in Fig. 14(b). The kinetics of $NaBH_4$ and KBH_4 hydrolysis catalyzed by cobalt chloride are similar, as it can be seen from the curves shown in Fig. 14(b). Two different slopes can be
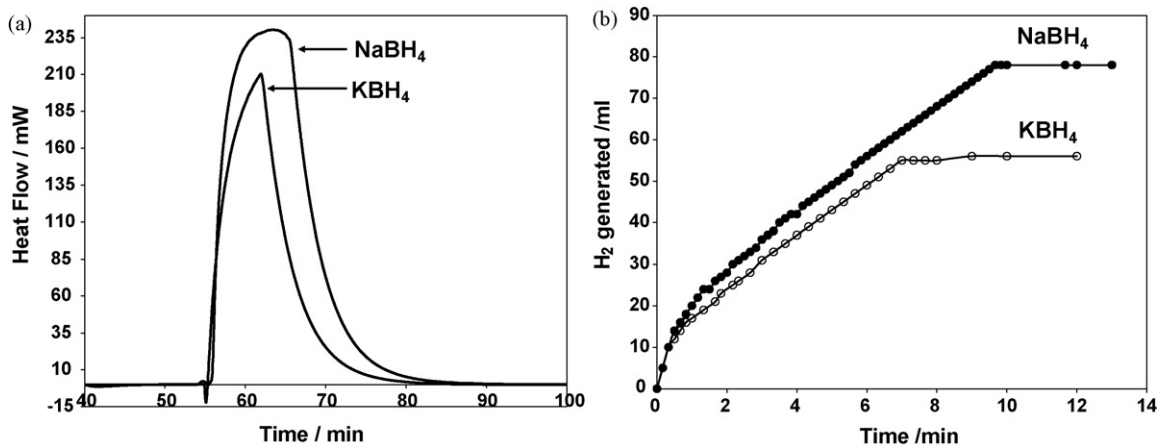

Fig. 14. $NaBH_4$ and KBH_4 hydrolysis reaction with $CoCl_2$ as catalyst: (a) evolved heat signal versus time; (b) H_2 generated as a function of time.
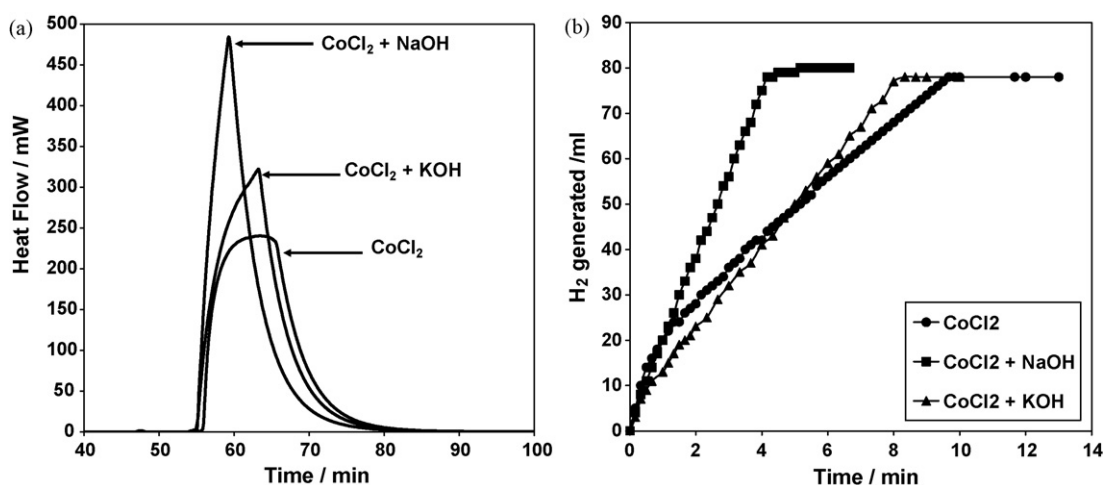
Fig. 15. NaBH$_4$ hydrolysis reaction with CoCl$_2$ as catalyst and 0.5 wt% of NaOH and KOH: (a) evolved heat signal versus time; (b) H$_2$ generated as a function of time.

observed, indicating that the reaction rate is faster at the beginning. Indeed, the H$_2$ generation rates, for both NaBH$_4$ and KBH$_4$, after a very high initial value of about 30 ml min^{-1}, i.e. 10 l min^{-1} g^{-1} of Co, decreased to 6 ml min^{-1}, i.e. 2 l min^{-1} g^{-1} of Co, and this value remained constant until a sharp decrease at the end of reaction.

After the hydrolysis, when stirring was stopped and calorimetric cell opened, black powders were visually observed at the bottom of the reaction cell. It is known that formation of black cobalt boride precipitate is instantaneous when cobalt chloride is used as catalyst and results in the high initial hydrogen generation rate [35]. The same behaviour has been detected in our experiments. The subsequent decrease in the activity of this catalyst is explained by the aggregation of the cobalt boride particles [35], which lowers the surface area of the catalyst hence limiting the catalytic activity.

The heat flow evolved during the hydrolysis reaction of NaBH$_4$ in the presence of cobalt chloride solution and 0.5 wt% of hydroxides (NaOH and KOH) is shown in Fig. 15(a). The obtained values for evolved heats were -236 kJ mol$_{NaBH_4}^{-1}$ and -230 kJ mol$_{NaBH_4}^{-1}$ in the presence of NaOH and KOH, respectively. These values are higher than in the case of NaBH$_4$ hydrolysis reaction without hydroxides. 100% of conversion was accomplished after 6 min with addition of NaOH, while the presence of KOH did not have significant influence on the reaction rate since the reaction time was 8 min. Hence, the higher [OH$^-$] concentration resulted in a more prominent increase of the rate of NaBH$_4$ hydrolysis reaction kinetics in the case of addition of NaOH compared to the same amount of KOH, Fig. 15(b).

The experimental calorimetric curves obtained for the hydrolysis reaction of KBH$_4$ in the presence of cobalt chloride solution and 0.5 wt% of hydroxides (NaOH and KOH) are shown in Fig. 16(a). The obtained values for the evolved heats were -207 kJ mol$_{KBH_4}^{-1}$ and -199 kJ mol$_{KBH_4}^{-1}$ in the presence of NaOH and KOH, respectively. While 100% of conversion was accomplished after 5 min with the addition of NaOH, the presence of KOH decreased the reaction rate (in particular for the reaction after the fast initial phase, see Fig. 16(b) when the slope of the curve changes), so the total reaction time was 11 min. An explanation could be a higher viscosity of the reaction mixture.

Compared to the other Co-based catalysts investigated in this work, the cobalt chloride solution shows significantly higher catalytic activity due to the initial acidic catalysis and the fine cobalt boride formed, which is agreement with reports in the literature [6,9]. The reduction of Co-based solids is much slower than in the case of cobalt chloride solution. The results obtained for the cobalt chloride solution activity are comparable with results for Co nanoparticles. Hence, optimizing the surface area and particle size of the catalyst as well as the pH of the solution for NaBH$_4$ and KBH$_4$ hydrolysis will improve the catalytic activity of the materials used as catalysts and allow the utilization of these systems for on demand hydrogen generation.

This study shows that presented calorimetric method can be successfully used in the measurement of evolved heat during hydrolysis reaction, thus providing important information for safety issues in industrial application of this reaction. The
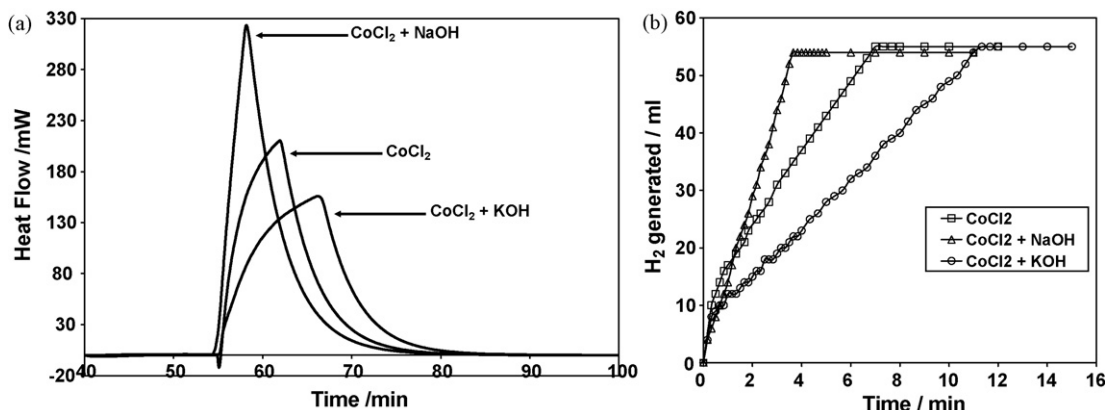

Fig. 16. KBH$_4$ hydrolysis reaction with CoCl$_2$ as catalyst and 0.5 wt% of NaOH and KOH: (a) evolved heat signal versus time; (b) H$_2$ generated as a function of time.

theoretical enthalpy of $NaBH_4$ hydrolysis reaction differ from the measured heat for about $(272.1–236 \text{ kJ mol}^{-1})$ 32 kJ mol^{-1}, which is not a negligible value and it has to be taken in account for industrial applications. In the presence of Co catalysts, as there are more side reactions, it is impossible to obtain real value of heat using thermodynamics tables. Hence, the precise measurements of heat will provide valuable information for any kind of application.

4. Conclusion

$NaBH_4$ and KBH_4 hydrolysis reactions in the presence of different Co-based catalysts have been investigated by titration microcalorimetry. The heats evolved during the hydrolysis reaction have been determined, and the kinetics of the reaction was successfully followed thanks to a home-made modification of the Setaram Titrys microcalorimeter.

Co nanoparticles have shown the highest catalytic activity compared to the other investigated solid catalysts. The measured hydrogen generation rates obtained for Co nanoparticles and aqueous $CoCl_2$ solution were similar due to the fast formation of highly active cobalt boride phase. Co-based catalysts are a promising and cost-effective way of releasing hydrogen from sodium and potassium borohydrides on demand, and they could replace the more expensive noble metal catalysts. However, optimization of the surface area and particle size of the catalysts can significantly improve their activity for $NaBH_4$ and KBH_4 hydrolysis, and it is necessary step for the successful utilization of these systems.

Efficient measurements of heat evolved during borohydride hydrolysis reaction are of great importance for reactor design and can be achieved by calorimetry measurements, as shown in this study.

Acknowledgements

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