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Aluminum chloride for accelerating hydrogen generation from sodium borohydride

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ABSTRACT

The present research paper reports preliminary results about the utilization of anhydrous aluminum chloride ($AlCl_3$) for accelerating hydrogen generation through hydrolysis of aqueous solution of sodium borohydride ($NaBH_4$) at 80 °C. To the best of our knowledge, $AlCl_3$ has never been considered for that reaction although many transition metal salts had already been assessed. $AlCl_3$ reactivity was compared to those of $AlCl_3{\cdot}6H_2O$, AlF_3, $CoCl_2$, $RuCl_3$ and $NiCl_2$. With $AlCl_3$ and a $NaBH_4$ solution having a gravimetric hydrogen storage capacity (GHSC) of 2.9 wt.%, almost 100% hydrogen was generated in few seconds, i.e., with a hydrogen generation rate (HGR) of 354 $L\,min^{-1}\,g^{-1}$(Al). This HGR is one of the highest rates ever reported. Higher HGRs were obtained by mixing $AlCl_3$ with CoCl2, $RuCl_3$ or $NiCl_2$. For example, the system $RuCl_3$:$AlCl_3$ (50:50 mass proportion) showed a HGR > 1000 $L\,min^{-1}\,g^{-1}$(Ru:Al). The hydrolysis by-products (once dried) were identified (by XRD, IR and elemental analysis) as being $Al(OH)_3$, NaCl and $Na_2B(OH)_4Cl$ and it was observed that even in situ formed $Al(OH)_3$ has catalytic abilities with HGRs of 5 $L\,min^{-1}\,g^{-1}$(Al). All of these preliminary results are discussed, which concludes that $AlCl_3$ has a potential as accelerator for single-use $NaBH_4$-based storage system.

1. Introduction

Sodium borohydride ($NaBH_4$) has attracted much attention since the late-1990s [1]. It is regarded as a highly promising hydrogen storage material because of its high theoretical gravimetric hydrogen storage capacity (GHSC) of 10.8 wt.%. With respect to the GHSC targets for on-board vehicular applications set b the US Department of Energy (US DOE) [2] (i.e., 4.5, 6.0 and 9.0 wt.% by the years 2007, 2010 and 2015, respectively), 10.8 wt.% appears to be highly attractive. This is the first advantage of $NaBH_4$. A second advantage is that stored hydrogen can be generated by hydrolysis (that is an exothermic reaction), half of hydrogen being provided by water:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (1)$$

Actually many advantages about both $NaBH_4$ and its hydrolysis have been noticed [3]. However, $NaBH_4$ today suffers from some issues. First the ideal 10.8 wt.% value has never been reached because hydrolysis takes place in excess of water and the by-product sodium metaborate ($NaBO_2$) is hydrated, what gives the following hydrolysis reaction:

$$NaBH_4 + (2+x)H_2O \rightarrow NaBO_2{\cdot}xH_2O + 4H_2 \quad (2)$$

Second recycling $NaBO_2$ back to $NaBH_4$ is inefficient and expensive. Third storage through $NaBH_4$ is too expensive and do not meet the US DOE cost targets [2]. There are other issues, already cited elsewhere [3], but the presently cited ones are the most significant problems. These issues were used by the US DOE in November 2007 as the main arguments for recommending a no-go for $NaBH_4$ for on-board vehicular hydrogen storage [2].

Despite the US DOE recommendation, many papers about $NaBH_4$ are published yet. As many groups of researchers, we believe that $NaBH_4$ has still a potential as hydrogen storage material but rather in portable and niche applications [4]. Such applications could envisage lower GHSCs. For instance a GHSC of 6.7 wt.% was reported [5] and this value is one of the highest ever reported. Actually there is now no specific effort devoted to improve the effective GHSC of $NaBH_4$. Researchers' attention focuses much more on hydrogen generation efficiency that can be obtained with metal-based catalytic materials [3]. One may talk about a 'race' for the most efficient, cost-effective catalytic material. Sometimes one may even have the feeling that the subject of the published papers focuses much more catalysts rather than hydrogen storage. Catalytic results with metal salts, metal powders, alloys, supported metals, metal borides and so on were reported. In general it is quite difficult to compare the

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reactivity of the studied catalytic materials because of differences in the experimental conditions. Ruthenium and cobalt are the best metals but cobalt is now much more investigated because it is cost-effective and is as reactive as ruthenium in some experimental conditions (see, e.g., reference [6]).

Historically the first catalytic materials tested were the metal salts although these ones are generally viewed and utilized as catalyst precursors. Schlesinger et al. [7] studied the effect of metal salts like $CoCl_2$ and $NiCl_2$ on $NaBH_4$ hydrolysis. Kaufman and Sen [8] found that the catalytic activity of metal salts was dependent on the cation (Co^{2+}, Cu^{2+} and Ni^{2+}) while it was independent of the anion (Cl^-, $NO_3{}^-$ and $CH_3CO_2{}^-$). In terms of hydrogen generation rates, Brown and Brown [9] reported about 85 $L\,min^{-1}\,g^{-1}$(metal) for both $RuCl_3$ and $RhCl_3$. Liu et al. [5] reported a rate of about 11 $L\,min^{-1}\,g^{-1}$(Co) for $CoCl_2$. This kind of catalytic accelerators is especially useful for hydrolyzing $NaBH_4$ stored as solid [5] or as gel [10]. Aqueous solution of, e.g., $CoCl_2$ can be added, in controlled amount, to either solid $NaBH_4$ [5] or $NaBH_4$ gel [10]. Another possibility is to premix $NaBH_4$ and, e.g., $CoCl_2$ [11] and then to add a controlled amount of pure water for starting hydrolysis. A last, but unlikely in application, possibility is to mix controlled amounts of $NaBH_4$ aqueous solution and, e.g., $CoCl_2$ aqueous solution [9]. In our opinion, metal salts are potential hydrolysis accelerators and because they have such potential they should not be neglected in searching for efficient catalytic materials. Up to now many transition metal salts have been studied but to the best of our knowledge aluminum salts and especially aluminum chloride ($AlCl_3$) have never been reported.

The present paper reports preliminary experimental results about catalytic abilities of $AlCl_3$ for accelerating hydrogen generation from $NaBH_4$ (hydrolysis). $AlCl_3$ showed very high reactivity. Hydrogen generation was very quick. One can even talk about one of the quickest hydrogen generations we ever observed with our various catalytic materials. $AlCl_3$ has a great potential and this is what the present paper reports. Nevertheless its reactivity has to be optimized because although our research activities focus reactive metal-based catalytic materials $AlCl_3$ is maybe too reactive. This is especially discussed.

2. Experimental

$AlCl_3$ (Aldrich), $AlCl_3{\cdot}6H_2O$ (Aldrich), AlF_3 (Aldrich), $CoCl_2$ (Aldrich), $RuCl_3$ (Strem) and $NiCl_2$ (Aldrich) were used as accelerators. The materials were used as received, except for $AlCl_3$. $AlCl_3$ grains were ground and sieved (64–125 μm). All of them were systematically handled in a glove box (under argon).

Hydrogen generation experiments were as follows. An equivalent of 14 mg of metal (Al, Co, Ru or Ni) was weighted, transferred into a tube (16 mm diameter), which was sealed thanks to a silicon septum. For the bimetallic systems like, e.g., Al:Co, the metals weight was kept at 14 mg while the respective proportions of each metal were varied. In parallel, an amount of 400 mg of $NaBH_4$ (Acros Organics 99%, powder) was weighted and transferred into a 5 mL sample flask under argon (glove box). The ratio metal/(metal + $NaBH_4$) was 10 wt.% (even for the bimetallic systems). Water (2.5 mL) was added to $NaBH_4$ just few seconds before injecting it over the catalytic accelerator. The GHSC of the $NaBH_4$ fuel was of 2.9 wt.%. The self-hydrolysis of $NaBH_4$ in water (in the absence of any accelerator) was <1 $mL\,min^{-1}$ at room temperature. Hydrogen volume generated by self-hydrolysis was therefore negligible. The hydrolysis temperature was set at 80 °C and this temperature was maintained thanks to a water bath (±1 °C). The room temperature was about 19 °C. The aqueous solution of $NaBH_4$ (0.79 mL) was then injected into the tube. The outlet tube exhaust was connected to a water-filled inverted burette (blue colored water). There was no stirring in the kinetic experiments, except for the stirring action of the evolved hydrogen [12]. Volume of generated hydrogen was measured by this way and was video-recorded in order to facilitate the data collecting. In the meantime the in situ reaction temperature was video-recorded by a thermocouple kept in the core of the reactor (tube). The initial hydrogen generation rate, abbreviated HGR, was calculated in $L\,min^{-1}$ or $L\,min^{-1}\,g^{-1}$(metal) at conversions <50% in agreement with the calculation procedure set by Komova et al. [13]. The total conversion (%), abbreviated here TC, was calculated as $100 \times (V_{max}/V_{th})$, where V_{max} is the effective volume of hydrogen produced (L) at the end of the experiment and V_{th} is the theoretical volume of hydrogen generated (L) if 100% TC. The TC is given with an experimental error of ±3%.

Hydrolysis reaction by-products were characterized by X-ray diffraction (Bruker D5005 powder diffractometer), by infrared spectroscopy (FTIR Nicolet 380) and by elemental analysis (performed at Service Central d'Analyses of CNRS, Vernaison, France).

3. Results and discussion

3.1. $AlCl_3$ reactivity

$NaBH_4$ hydrolysis can be accelerated by either metals salts or acids [7]. Kaufman and Sen [8] suggested that the overall hydrogen generation in the presence of metal salts is simultaneously metal-catalyzed:

$$4M^{2+} + 8H_2O \rightarrow 4M(OH)_2 + 8H^+ \tag{3}$$

$$BH_4{}^- + 4M(OH)_2 \rightarrow B(OH)_4{}^- + 4M^0 + 4H_2O \tag{4}$$

and acid-catalyzed:

$$BH_4{}^- + 4M^{2+} + 3H_2O \rightarrow B(OH)_3 + 4M^0 + 7H^+ \tag{5}$$

$$7BH_4{}^- + 7H^+ + 21H_2O \rightarrow 7B(OH)_3 + 28H_2 \tag{6}$$

Keeping in mind these reactions, our objective was to find a salt that could react promptly with water while generating protons. Since many of the transition metals had been assessed, we decided to consider the p-group metals. $AlCl_3$ stood out (often used as precursor for preparing aluminum hydroxide and then aluminum oxide). It is known to react vigorously with water:

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl \tag{7}$$

The reaction is exothermic and generates protons, both features being useable for hydrolyzing $NaBH_4$ and so generating hydrogen. Another significant interest with Al is its low cost in relation to both Co and Ru. Hence in order to benefit from both features solid $AlCl_3$ was used. Aqueous solution of $NaBH_4$ was then added into the reactor containing solid $AlCl_3$. The same procedure was applied for each metal salt, which was chosen for specific reasons: that is, $AlCl_3{\cdot}6H_2O$ in order to check the hydration effect on $AlCl_3$ reactivity; AlF_3 to compare the effect of the anion (Cl^- versus F^-) on reactivity; $RuCl_3$ and $CoCl_2$ because they are among the most reactive and most studied metal salts; $NiCl_2$ because having to be used as a component of bimetallic systems.

Table 1 reports the HGRs reached by each of the metal salts at 80 °C. The temperature of 80 °C was chosen because it is the working temperature of a polymer electrolyte membrane fuel cell. $AlCl_3$ is highly reactive with a HGR of 354 $L\,min^{-1}\,g^{-1}$(Al) (Fig. 1). It is followed by $RuCl_3$, $CoCl_2$, $AlCl_3{\cdot}6H_2O$, $NiCl_2$ and AlF_3. $AlCl_3$ high reactivity was accompanied with a pronounced increase in temperature since it increased of 18 °C in few seconds. The water bath was quite ineffective in that case. $RuCl_3$ and $CoCl_2$ confirmed their high reactivity [7] with HGRs above 100 and 80 $L\,min^{-1}\,g^{-1}$(metal), respectively. $NiCl_2$ was quite interesting with a HGR of 39 $L\,min^{-1}\,g^{-1}$(Ni). AlF_3 were deceiving in relation to $AlCl_3$. The highly exothermic solubility and hydration of the latter may explain such reactivity

Table 1
Hydrogen generation rates (HGRs) reached by $AlCl_3$, $AlCl_3{\cdot}6H_2O$, AlF_3, $CoCl_2$, $RuCl_3$ and $NiCl_2$ at 80 °C.

	HGR ($L\,min^{-1}$)	HGR ($L\,min^{-1}\,g^{-1}$(metal))	$\Delta T/t$[a] (°C)/(s)	TC[b] (%)
$AlCl_3$	4.95	354	18/4	98
$AlCl_3{\cdot}6H_2O$	1.00	71	9/4	49
AlF_3	0.19	13	3/13	n.a.[c]
$CoCl_2$	1.14	81	8/8	79
$RuCl_3$	1.44	103	9/4	88
$NiCl_2$	0.55	39	6/9	81

[a] Increase in temperature in the core of the reactor/time to reach ΔT.
[b] TC as total conversion.
[c] Not assessed.

difference. With AlF_3, the temperature increased of only 3 °C. There was thus an anion effect in our experimental conditions and this observation contradicts Kaufman and Sen's [8]. $AlCl_3{\cdot}6H_2O$ showed high reactivity but much less than that of $AlCl_3$. This implies that $AlCl_3$ is more reactive because it is anhydrous. From these results, it appears that $NaBH_4$ hydrolysis takes advantages of both exothermic dissolution of $AlCl_3$ and protons generation.

Hence our preliminary tests show that $AlCl_3$ has a potential as accelerator of $NaBH_4$ hydrolysis. The catalytic ability of $AlCl_3$ is in the range of the highest values reported so far in the literature [3]. Note that Gonzales et al. [14] reported that the presence of a metal chloride boosts $NaBH_4$ decomposition. Interestingly it was observed that the reaction was violent and according to the authors this raises a serious safety concern. In our opinion the reaction cannot be called as violent because it is a common objective to find highly reactive catalytic materials [3]. Further, catalysts with HGRs above 500 $L\,min^{-1}\,g^{-1}$(metal) have already been synthesized [15].

Table 1 also shows the TCs. A TC of almost 100% was observed with $AlCl_3$. The TCs were almost similar for the other salts, with values in the range 80–90%, except for $AlCl_3{\cdot}6H_2O$ (not determined for AlF_3). In fact the comparison the TCs is not really relevant because of discrepancies in the hydrolysis reaction medium. As it will be shown below, $AlCl_3$ is transformed to specie that has a non-negligible catalytic ability towards $NaBH_4$. Accordingly all of the $NaBH_4$ molecules are hydrolyzed (Fig. 1).

3.2. By-products

After the hydrolysis, the reaction by-products were recovered and visually observed. With $CoCl_2$ and $RuCl_3$, black powders were recovered at the bottom of the reactor [7,9]. It is generally admitted that cobalt boride [7] and ruthenium [9] form in such experimental conditions (i.e., reduction by $NaBH_4$). For $AlCl_3$, the remains of hydrolysis were visually different. A white matrix was recovered. It was dried under vacuum at room temperature. A white powder was obtained. Elemental analysis showed the presence of Al, B, Cl, and Na. The powder was then characterized by X-ray diffraction (Fig. 2). Sodium chloride NaCl and sodium boron chloride hydroxide $Na_2B(OH)_4Cl$ were identified. The powder was also analyzed by IR (Fig. 3). The wide band observed in the region 3000–3600 cm^{-1} was caused by the stretching of O–H. The band at approximately 1620 cm^{-1} was the deformation mode H–O–H of molecular water absorbed. The solid was hydrated. Bands characteristics of B–O and Al–O vibrators (in the region 500–1500 cm^{-1}) were identified. The observations from the IR spectrum are consistent with those from the X-ray diffraction pattern.

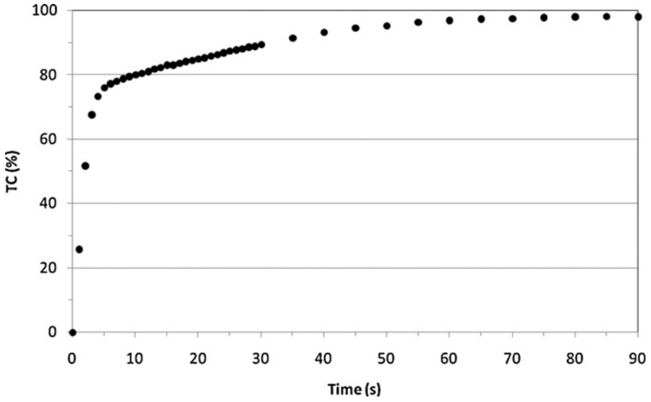

Fig. 1. Hydrogen generation (TC in %) versus time (s) for $AlCl_3$-accelerated hydrolysis of $NaBH_4$ at 80 °C.

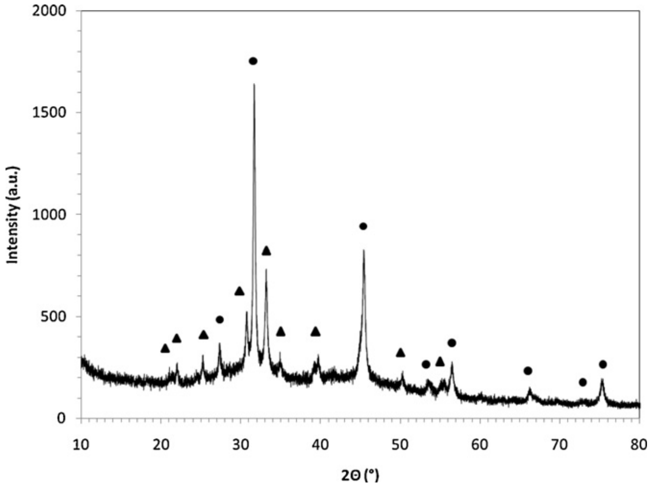

Fig. 2. XRD pattern of by-products of $AlCl_3$-accelerated hydrolysis (circles NaCl ref. pattern 01-072-1662; triangles $Na_2B(OH)_4Cl$ ref. pattern 00-011-0012).

The powder was then washed five times in order to eliminate both NaCl and $Na_2B(OH)_4Cl$. The washed white powder was dried under vacuum at room temperature. By X-ray diffraction, no peak was revealed (pattern not given). The washed/dried powder was then analyzed by elemental analysis (Al, Na, Cl, B had been analyzed but not O and H). The presence of only Al was detected. These observations were consistent with Eq. (7) and suggested the formation of $Al(OH)_3$.

$Al(OH)_3$ is not a compound known for its catalytic abilities. In order to assess its reactivity, successive shots of $NaBH_4$ solution

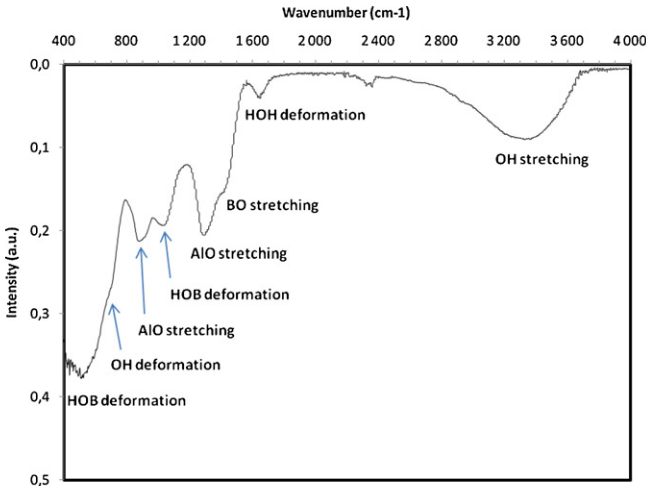

Fig. 3. IR spectrum of by-products of $AlCl_3$-accelerated hydrolysis.

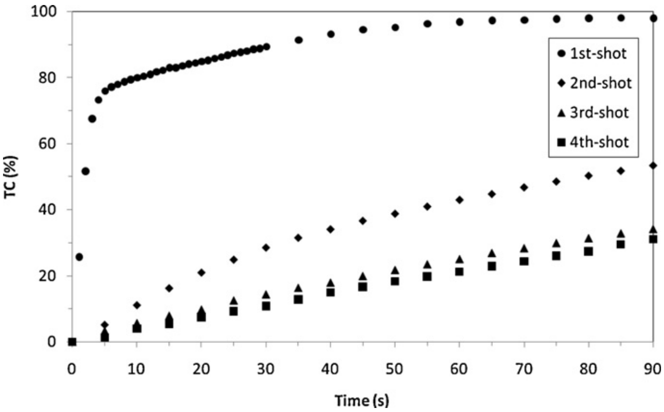

Fig. 4. Hydrogen generation (TC in %) versus time (s) for successive shots over $AlCl_3$ (first shot) and $Al(OH)_3$ (second, third, and fourth shots) at 80 °C.

were carried out. Typically at the end of the first hydrolysis (i.e., with $AlCl_3$), 0.79 mL of $NaBH_4$ solution was injected in the reactor (over the remains of the first hydrolysis) and the hydrogen generation was measured (Fig. 4). Table 2 reports the HGRs for four successive shots over $AlCl_3$ (first shot) and then $Al(OH)_3$ (second, third and fourth shots). After the first shot, the HGR was dramatically decreased from 354 to 8 and then to 5 $L\,min^{-1}\,g^{-1}$(Al). In parallel another experiment was carried out. After a first shot with $AlCl_3$, $Al(OH)_3$ was recovered and after a washing–drying process it was tested. A HGR of 5 $L\,min^{-1}\,g^{-1}$(Al) was observed. This value was similar to those obtained for the successive third and fourth shots. Accordingly the value 5 $L\,min^{-1}\,g^{-1}$(Al) characterizes the catalytic abilities of in situ formed $Al(OH)_3$. This observation justifies the 100% conversion observed with $AlCl_3$ (Table 1 and Fig. 1).

These results show that $AlCl_3$ should be much more regarded as a single-use accelerator [10,11] rather than a multi-use catalyst [1] (discussed more in details in Section 3.5).

3.3. Parameters variations

The increase of the internal reactor temperature at the early seconds of the hydrolysis did not permit to perform a reliable determination of apparent activation energy (E_A) for $AlCl_3$. For example, it was observed a temperature variation of 70 °C (in 3 s) for a hydrolysis set initially at 20 °C despite the presence of a water bath. Hence in such conditions hydrolysis was activated by $AlCl_3$ as well as by the high temperature increase [14]. Table 3 shows the HGRs for experiments at initial temperatures of 20, 40, 60 and 80 °C. As expected, the HGR increased with temperature. However, the increase of the reactor temperature was too important at each reaction and thus the HGR could not to be used for estimating apparent activation energy. High reactivity is in general problematic for fundamental studies (kinetics, mechanisms and so on). To the best of our knowledge, such a situation has only been reported by Gonzales et al. [14], but never in papers reporting catalytic materials having shown HGRs of hundreds $L\,min^{-1}\,g^{-1}$(metal). This asks then a question: how was the reactor temperature controlled with such catalytic materials? In our experimental conditions, such operation seemed to be impossible. This asks then another question: how will be managed such temperature variations in real applications? Note that Gonzales et al. [14] reported an increase of pressure in addition to the increase of temperature.

Table 2
HGR for successive shots over $AlCl_3$ (first shot) and $Al(OH)_3$ (second, third, and fourth shots) at 80 °C.

	HGR ($L\,min^{-1}\,g^{-1}$(Al))	$\Delta T/t$[a] (°C)/(s)	TC (%)
Shot 1—$AlCl_3$[b]	354	18/4	98
Shot 2—$Al(OH)_3$	8	1/30	94
Shot 3—$Al(OH)_3$	5	0/0	97
Shot 4—$Al(OH)_3$	5	0/0	95

[a] Increase in temperature in the core of the reactor/time to reach ΔT.
[b] From Table 1.

Table 3
$AlCl_3$ reactivity at various temperatures.

T (°C)	HGR ($L\,min^{-1}\,g^{-1}$(Al))	$\Delta T/t$[a] (°C)/(s)	TC (%)
20	297	70/3	100
40	305	44/2	97
60	324	26/2	94
80[b]	354	18/4	98

[a] Increase in temperature in the core of the reactor/time to reach ΔT.
[b] From Table 1.

The initial amount of $AlCl_3$ was tentatively varied (14, 20, 25 and 30 mg of Al) and the HGRs were determined at 80 °C (Table 4). The HGRs and the amounts of Al are consistent since plotting ln(HGR) as a function of ln([Al]) gives a slope of 1. Our calculations showed that the effect of the temperature variation on the constant $-E_A/RT$ was rather negligible (variations of about 10%) and that the slope of 1 was almost unaffected. A value of about 1 was often reported for metal catalysts [16–18] as that can be expected for catalysts.

Table 4 shows the mole ratios $NaBH_4$/Al, $NaBH_4/H^+$ (H^+ stem from $AlCl_3$; Eq. (7)), H^-/H^+ and H_2O/Al. The ratios H^-/H^+ were well above 1. Hence it is obvious that the $AlCl_3$-accelerated hydrolysis is a complex reaction [8], involving certainly various hydrolysis: i.e., acid-catalyzed (H^+ from $AlCl_3$), self-hydrolysis activated by the temperature increase, $Al(OH)_3$-catalyzed and perhaps Al^{3+}-catalyzed. All of these reactions might compete but at present it is quite difficult to assess the contribution of each. Further investigations are needed.

The initial amount of $NaBH_4$ was besides tentatively varied (63, 95, 126 and 158 mg). Both HGRs and TCs were determined at 80 °C (Table 5). The reaction order versus $NaBH_4$ was determined by plotting ln(HGR) as a function of ln([$NaBH_4$]). It was −0.5. This negative order is consistent with some published studies [19–21]. Negative, positive and zero orders were reported for $NaBH_4$ [18]. In our experimental conditions, a negative order was expectable because increasing the $NaBH_4$ amount made the hydrolysis occurrence much harsher.

Due to the facts that $AlCl_3$ was too much reactive and that its contact with $NaBH_4$ aqueous solution was accompanied with a significant increase of the temperature, performing a kinetic study proved difficult. It appeared to be irrelevant to determine apparent activation energy. Nevertheless it was tentatively determined reaction orders versus $AlCl_3$ and $NaBH_4$, which were of 1 and −0.5, respectively. Such values are quite consistent with data reported throughout the open literature [18].

3.4. Bimetallic systems

Raney catalysts are metal alloys composed of a metal like, e.g., Ni or Co and of Al (in proportions >90 and <10%, respectively). They are used in various processes including, e.g., hydrogenations and dehydrogenations. Raney Ni and Raney Co, commercially available, have been assessed for hydrolyzing $NaBH_4$. Liu et al. [22] studied Raney Ni, Raney Co, Raney $Ni_{25}Co_{75}$, Raney $Ni_{50}Co_{50}$ and Raney $Ni_{75}Co_{25}$. HGRs of 0.3–1.5 $L\,min^{-1}\,g^{-1}$(catalyst) were reported at 20 °C and for a $NaBH_4$ solution with a GHSC of 0.2 wt.%. Doping a metal with Al may improve the catalytic performances of the metal. This is the purpose of the study reported in the present section.

Rather than synthesizing alloys, mechanical mixtures of $AlCl_3$ with a metal salt MCl_x were prepared. MCl_x were $CoCl_2$, $RuCl_3$ and

Table 4
$AlCl_3$ reactivity for various initial Al amounts at 80 °C.

m(Al) (g)	$NaBH_4$/Al (mol/mol)	$NaBH_4/H^{+}$[a] (mol/mol)	H^{-}/H^{+}[b] (mol/mol)	H_2O/Al (mol/mol)	HGR [c]	Δ*T*/*t*[d] (°C)/(s)	TC (%)
14[e]	6.4	2.1	8.4	85	354	18/4	98
20	4.5	1.5	6.0	59	552	26/4	96
25	3.6	1.2	4.8	47	685	37/2	94
30	3.0	1.0	4.0	40	774	45/6	96

[a] H^+ from $AlCl_3$; Eq. (7).
[b] H^- from $NaBH_4$.
[c] In $L\,min^{-1}\,g^{-1}$(Al).
[d] Increase in temperature in the core of the reactor/time to reach Δ*T*.
[e] From Table 1.

Table 5
$AlCl_3$ reactivity for various initial $NaBH_4$ amounts at 80 °C.

m($NaBH_4$) (mg)	$NaBH_4$/Al (mol/mol)	$NaBH_4/H^{+}$[a] (mol/mol)	H^{-}/H^{+}[b] (mol/mol)	H_2O/Al (mol/mol)	HGR[c]	Δ*T*/*t*[d] (°C)/(s)	TC (%)
63	3.2	1.1	4.4	85	520	35/3	100
95	4.8	1.6	6.4	85	429	24/3	97
126[e]	6.4	2.1	8.4	85	354	18/4	98
158	8.1	2.7	10.8	85	336	19/3	96

[a] H^+ from $AlCl_3$; Eq. (7).
[b] H^- from $NaBH_4$.
[c] In $L\,min^{-1}\,g^{-1}$(Al).
[d] Increase in temperature in the core of the reactor/time to reach Δ*T*.
[e] From Table 1.

$NiCl_2$. MCl_x and $AlCl_3$ were mixed in a mortar under argon (in glove box). Various proportions (denoted by α, in mass) of MCl_x and $AlCl_3$, denoted $MCl_x{}^{\alpha}$:$AlCl_3{}^{100-\alpha}$, were used (Table 6). Anyway the experimental conditions for carrying out the $NaBH_4$ hydrolysis were identical to those described in Section 2.

The experiments were started on with $CoCl_2$. Note that the performances reported hereafter are systematically compared to that of $CoCl_2$ (Table 1). First, a 90:10 mixture, close of that of Raney Co, was tested. $CoCl_2{}^{90}$:$AlCl_3{}^{10}$ showed a HGR of 309 $L\,min^{-1}\,g^{-1}$(Co:Al). The performance was greatly improved although less high than that of $AlCl_3$. Second, the proportion (in mass) of $AlCl_3$ was increased. $CoCl_2{}^{75}$:$AlCl_3{}^{25}$ was prepared and tested. Its HGR was similar to that of $CoCl_2{}^{90}$:$AlCl_3{}^{10}$. Third, the $AlCl_3$ proportion (in mass) was further increased. $CoCl_2{}^{50}$:$AlCl_3{}^{50}$ overpassed the previous bimetallic systems with a HGR of 428 $L\,min^{-1}\,g^{-1}$(Co:Al). The improved reactivity may be ascribed to $AlCl_3$. Fourth, a further increase of $AlCl_3$ proportion (in mass) led to a HGR of 453 $L\,min^{-1}\,g^{-1}$(Co:Al). To summarize, improved reactivity was obtained by mixing $CoCl_2$ and $AlCl_3$. Interestingly the evolution of the HGR with the proportion α follows a volcano-shape curve, with a maximum for $\alpha = 25$ (Fig. 5).

A second set of experiments was carried on with $RuCl_3$ and $AlCl_3$. Ru is highly reactive for hydrolyzing $NaBH_4$ [7,9] but it is an expensive metal. Reducing it content through mixing (or alloying) with a cheaper metal can be viewed as a solution for reducing the catalyst cost [23]. Hence $RuCl_3$ was tested in our study (Table 6). The system $RuCl_3{}^{50}$:$AlCl_3{}^{50}$ was highly reactive. The HGR was above 1000 $L\,min^{-1}\,g^{-1}$(Ru:Al). Mixing $AlCl_3$ with $RuCl_3$ appears to be highly beneficial. A third set of experiments was performed with $NiCl_2$ and $AlCl_3$. In that case the main objective was to dope the catalytic abilities of Ni, a cheap metal. A shown in Table 6, the bimetallic system was more performing than $NiCl_2$. In short, $AlCl_3$ addition to MCl_x is in most cases beneficial.

The reactivity data discussed in the present section are preliminary results. It is mainly showed that the addition of $AlCl_3$ to MCl_x is beneficial in terms of HGR and cost. Further investigations should provide improvements. Actually the present results could be a basis for synthesizing Co-, Ni- or Ru-based alloys involving Al as it is the case for Raney metals. This has already been envisaged even if it was via a different approach. Soler et al. [24] reported hydrogen generation through reaction of Al with $NaBH_4$ in aqueous media. It was especially shown that aluminum alloys like, e.g., Al/Si and Al/Co are efficient systems for decomposing $NaBH_4$. Metal salt is a potential accelerator for single-use storage system but unlikely for multi-use storage system. Because in the latter case catalyst has to catalyze each time it is in contact with fresh $NaBH_4$ solution and thus alloys appears to be more convenient than are salts. With that view Al has a high potential.

Table 6
Bimetallic systems.

	HGR ($L\,min^{-1}\,g^{-1}$(metals))	TC (%)
$CoCl_2{}^{90}$:$AlCl_3{}^{10}$	309	100
$CoCl_2{}^{75}$:$AlCl_3{}^{25}$	306	98
$CoCl_2{}^{50}$:$AlCl_3{}^{50}$	428	100
$CoCl_2{}^{25}$:$AlCl_3{}^{75}$	453	100
$RuCl_3{}^{50}$:$AlCl_3{}^{50}$	1032	100
$RuCl_3{}^{25}$:$AlCl_3{}^{75}$	864	100
$NiCl_2{}^{50}$:$AlCl_3{}^{50}$	357	95
$NiCl_2{}^{25}$:$AlCl_3{}^{75}$	403	92

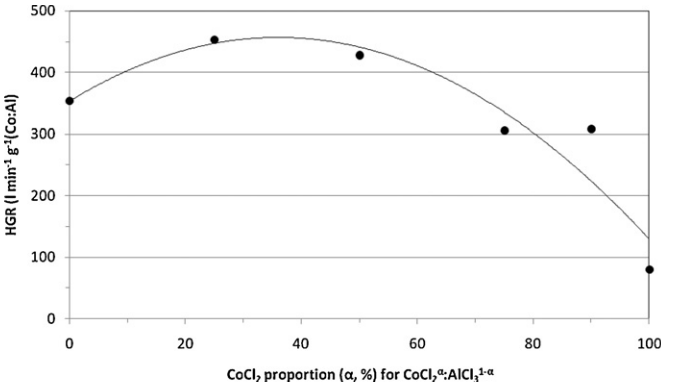

Fig. 5. Evolution of the HGR with α for the bimetallic system $CoCl_2{}^{\alpha}$:$AlCl_3{}^{1-\alpha}$.

3.5. Application perspectives

As discussed in Section 1, the US DOE has recommended a no-go for $NaBH_4$ for automotive hydrogen storage [2]. Nevertheless the decision has not considered, e.g., portable applications. Investigations for improving $NaBH_4$ storage for this kind of applications are currently in progress in several research laboratories throughout the world. Among the catalytic systems, metal salts like, e.g., $CoCl_2$ are sometimes tested [10]. In the perspective of portable applications, $AlCl_3$ (or bimetallic systems) may be also envisaged.

In our experimental conditions, the GHSC of our $NaBH_4$ aqueous solution was 2.9 wt.%. In order to increase the GHSC, the volume of water had to be decreased. Molar ratio $H_2O/NaBH_4$ of 4 was then envisaged (this ratio is in fact the solubility limit of $NaBH_4$ in water, i.e., 55 g per 100 g [25]). This corresponds to a theoretical GHSC of 7.3 wt.%. With $AlCl_3$ as accelerator, a HGR of 278 $L\,min^{-1}\,g^{-1}$(Al) was observed (determined at a conversion of 25%) but the TC was only of 32%. This means an effective GHSC of only 2.3 wt.%. Molar ratio $H_2O/NaBH_4$ of 7 (theoretical GHSC of 4.9 wt.%) was also considered. The TC was 58% (i.e., effective GHSC of 2.8 wt.%). For both molar ratios, the concentration of $NaBO_2$ that could be formed was above its solubility in water (i.e., 28 g per 100 g). The $NaBO_2$ precipitation may explain the low conversions observed for these experiments [25]. Hence further improvements are necessary in order to increase the effective GHSC. For that alternate storage ways could be regarded [5,10].

Amendola et al. [1] suggested a calculation for estimating achievable power levels from hydrogen generators. Their calculation can be accurately applied to our results. Let us cite Amendola et al. [1] accurately. "Assuming a [. . .] fuel cell operates at ≈0.7 V, generating 1 $g(H_2)\,min^{-1}$ is equivalent to [. . .] 1125 W, i.e., 1 $L\,min^{-1}$ can power a 100-W fuel cell." In our case, the various $AlCl_3$-based accelerators could produce, in our experimental conditions, the equivalent of 35–100 $kW\,g^{-1}$(metal). It is obvious that so high performances let certain flexibility in hydrogen generation, given that portable applications only need tens-W powers.

4. Conclusion

The present study has shown the potential of $AlCl_3$ as catalytic accelerator of $NaBH_4$ hydrolysis. $AlCl_3$ is highly reactive and in our experimental conditions surpasses both $RuCl_3$ and $CoCl_2$. At 80 °C, $AlCl_3$ accelerated the generation of all of the stored hydrogen in few seconds (350 $L\,min^{-1}\,g^{-1}$(Al)). This HGR is one of the highest rates ever reported in the open literature. The hydrolysis was accompanied with a significant increase of the temperature and that complicated the realization of any kinetic study. The reaction by-products (once dried) were identified as being $Al(OH)_3$, NaCl and $Na_2B(OH)_4Cl$. Then it was envisaged to mix $AlCl_3$ with another metal salt such as $CoCl_2$, $RuCl_3$ and $NiCl_2$. Much higher HGRs were measured. For example, for the system $RuCl_3{}^{50}$:$AlCl_3{}^{50}$, a HGR of about 1000 $L\,min^{-1}\,g^{-1}$(Ru:Al) was obtained. To the best of our knowledge, it is certainly the highest rate ever reported in the open literature.

From these preliminary results, it has been concluded that $AlCl_3$ has a potential as accelerator for single-use storage system. However, for multi-use storage system, catalyst has to be utilized many times, that is, at each time it is in contact with fresh $NaBH_4$ solution. In that case, alloys seem to be more convenient than salts. On the basis of the performances reported, it appears that $AlCl_3$ could be used as raw material for preparing such alloys. Doping, e.g., Co or Ru with Al might improve performances and also decrease catalyst cost. Such investigations are in progress.

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