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Ru-based bimetallic alloys for hydrogen generation by hydrolysis of sodium tetrahydroborate

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Abstract

The present study contemplates the application of Ru-based bimetallic alloys for hydrogen generation by hydrolysis of sodium tetrahydroborate (NaBH₄). Ru and Pt, RuCu, RuPd, RuAg and RuPt (atomic ratio 1:1), PtAg, and Ru_xPt_y (atomic ratios *x*:y of 2:1 or 1:2), all supported over titanium oxide, were prepared. Their activity decreased in the order Ru~Ru₂Pt₁ > RuPt~Ru₁Pt₂ > RuPd > RuAg~Pt > RuCu > PtAg. Alloying Ru with an inactive metal like Cu, Pd or Ag did not improve the performances of Ru. The catalytic ability of Ru₂Pt₁-TiO₂ is in the range of the highest values reported so far in the literature with a hydrogen generation rate of 15.2 L(H₂) min⁻¹ g⁻¹(RuPt). After separation from the reaction medium and rinsing with deionised water, the used Ru₂Pt₁-TiO₂ catalyst was re-evaluated and almost the same catalytic activities as fresh catalyst were obtained during several cycles.

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1. Introduction

Sodium tetrahydroborate NaBH₄ is considered as a prospective safe chemical hydride for hydrogen storage [1]. Its hydrogen content is of 10.66 wt.%, what makes itself one of the highest hydrogen containing compounds. Molecular hydrogen can be recovered by thermal decomposition of NaBH₄ [1] but, to use its high hydrogen capacity, its hydrolysis reaction is the most attractive approach [2]. The hydrolysis reaction is generally written with the quantity of water just required to evolve hydrogen: NaBH₄ + 2H₂O \rightarrow NaBO₂ + 4H₂. Hence, 10.92 wt.% of hydrogen can be recovered. However, the by-product NaBO₂ is a compound that is usually hydrated and hydrolysis must involve four molecules of water [3], namely, NaBH₄ + 4H₂O \rightarrow NaB(OH)₄ + 4H₂. Hence, 7.34 wt.% of hydrogen can be recovered, what is smaller than the former value.

NaBH₄ is water-sensitive. On its own, it reacts exothermally with water: its self-hydrolyses [2]. The self-hydrolysis rate is

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a function of temperature and pH [4]. Controlled production of hydrogen can be obtained by buffering the aqueous solution of NaBH₄ at a high pH and then using a catalyst [2]. Catalysts are essential for controlled rate of hydrogen generation by NaBH₄ hydrolysis [5]. The catalysts used are transition metals and these ones have been used in various forms: metal salts [6]; metal borides [7]; La- and Ni-based intermetallic compounds (LaNi_{4.5}M_{0.5}, M: metal) [8]; fluorinated metals [9]; bulk metals [10]; Raney metals [11]; and, metal-promoted metal oxides [12]. Today, the main objective of the researchers is to find highly capable catalysts with superior activity and durability.

The best metals for hydrogen generation by hydrolysis of NaBH₄ are Ru, Rh and Pt. The order of these metals, made out from their catalytic activity, is somewhat different from one paper to the other, e.g., Ru~Rh>Pt [6]; Pt>Rh>Ru [12]; Rh>Pt~Ru [13]. An alternative way for searching for new catalysts could be the bimetallic alloys AB (where A would be Ru, Pt or Rh, and B another transition metal). For example, Krishnan et al. [14] noticed that the efficiency of PtRu was almost double of that of either Ru or Pt (all were supported over LiCoO₂). Liu et al. [11] observed that alloys Raney NiCo led to faster hydrogen generation rates than the pure metals and concluded "this kind of phenomenon is very interesting from a practical as well as academic point of view".

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The present paper reports the catalytic behaviour of Ru- and Pt-based bimetallic alloys supported over TiO_2 for hydrogen generation by hydrolysis of NaBH₄.

2. Experimental

Titanium oxide (Aeroxide[®] TiO₂ P25, Degussa, 55 m² g⁻¹) was chosen as support. Its X-ray diffraction (XRD) measurement was taken on a Bruker axs D8 advance powder diffractometer (Cu K α_1 radiation, $\lambda = 0.15406$ nm). TiO₂ had a mixed crystalline structure anatase-rutile in the proportions 80–20% (XRD pattern not given; the phase identification used the JCPDS index 89-4921 to reference the anatase peaks and the JCPDS index 89-4920 to reference the rutile peaks). The crystallite sizes were determined (from the XRD pattern) as being 24 and 37 nm for the anatase and rutile structures, respectively.

The wet impregnation of the metals was as follows. The desired amount of TiO₂ was wetted and the slurry pH was adjusted to 10 (0.5M NaOH solution). The desired amount(s) of the metal(s) (1 wt.%, atomic ratios of 1:1, 2:1 or 1:2) was(were) simultaneously added from aqueous solution(s) of the metallic salt(s) (CuCl₂, RuCl₃, Pd(NO₃)₂, AgNO₃, H₂PtCl₆ Strem). The mixture was stirred for 1 h and was dried in an oven for 12 h. The catalysts are denoted as Cu-TiO₂, Ru-TiO₂, Pd-TiO₂, Ag-TiO₂, Pt-TiO₂, RuCu-TiO₂, RuPd-TiO₂, RuAg-TiO₂, RuPt-TiO₂, Ru₂Pt₁-TiO₂, Ru₁Pt₂-TiO₂ and PtAg-TiO₂.

In typical hydrogen generation experiments (apparatus adapted from ref. [5]), 20 mL of an aqueous alkaline (NaOH, 1 M, Aldrich) solution of NaBH₄ (0.394 g, Aldrich) filled a sealed flask. The sealed flask was fitted with an outlet tube for collecting evolved hydrogen. An amount of 0.250 g of catalyst was added to the solution under stirring (not to have external diffusion effects, 400 rpm). The temperature was maintained within the range of (20.0 ± 0.5) °C thanks to a water bath. The outlet tube exhaust was connected to a water-filled graduated U-type glass cylinder and generated hydrogen was measured by monitoring water displacement from the cylinder as the reaction proceeded. The hydrogen generation rate (HGR) was then calculated in the time range 0–5 min. The relative error on the measured volume was of about 2%.

3. Results and discussion

3.1. Preliminaries

The self-hydrolysis rate of the aqueous solution of NaBH₄ was measured and was found as being $<0.01 \text{ mL}(\text{H}_2) \text{ h}^{-1}$ ($<0.2 \text{ }\mu\text{L}(\text{H}_2) \text{ min}^{-1}$), what is negligible.

HGR with metal-free TiO₂ was assessed. In our experimental conditions, it was of 0.07 mL(H₂) h^{-1} (1.2 μ L(H₂) min⁻¹). TiO₂ was inactive towards NaBH₄ hydrolysis.

3.2. Reactivity of the bimetallic alloys

Peña-Alonso et al. [15] have proposed a mechanism for the catalytic production of hydrogen from an aqueous solution of NaBH₄. This mechanism is partly given in Fig. 1. It involves two essential kinetic steps, namely, the tetrahydroborate dissociative chemisorption to the surface metal atoms and the transfer of the negative charge of $M-BH_3^-$ to H of M-H. The hydrogen evolution reaction may be summarised as follows: $(M-H+e^-)+HO^{\delta-}-H^{\delta+} \rightarrow M^{\bullet}+H_2+HO^-$ (and HO⁻ interacts then with adsorbed BH₃). A similar reaction mechanism has also been suggested by Guella et al. [16] for a Pd catalyst; the authors have claimed that the activation of the substrate towards hydrolysis is caused by electron-withdrawing and electron-releasing effects of the palladium atoms on the catalyst



Fig. 1. Mechanism for the catalytic production of hydrogen from an aqueous solution of NaBH₄; adapted from ref. [15].

surface via the putative chemiads orbed species $Pd-BH_3^-$ and Pd-H.

Nørskov and co-workers [17] have developed a systematic and affordable computational framework for the rational screening of over 700 bimetallic alloys for the hydrogen evolution reaction: $2\mathbf{H}^+ + 2e^- \rightarrow \mathbf{H}_2$. This reaction had been chosen by the authors for its chemical simplicity and it looks like the reaction $(\mathbf{M}-\mathbf{H}+e^-)+\mathbf{HO}^{\delta-}-\mathbf{H}^{\delta+}\rightarrow \mathbf{M}^{\bullet}+\mathbf{H}_2+\mathbf{HO}^-$ given above. For this reason, the present study uses the Nørskov and co-workers' work [17] as a 'tool' in order to attempt to predict the reactivity of the bimetallic alloys that will be selected.

Before preparing bimetallic alloys AB, it is essential to make a selection for A. Today, the best transition metals for hydrogen generation by NaBH₄ hydrolysis are known (see Section 1): they are Ru, Rh and Pt. On the basis of the Krishnan et al.'s work [14], which reports the catalytic abilities of Ru- and Pt-promoted LiCoO₂, it was decided to evaluate Ru and Pt (both supported over TiO₂). Fig. 2 shows the relations of generated hydrogen volume with time for both supported metals. The HGRs were of 38.8 and 9.1 mL min⁻¹ for Ru-TiO₂ and Pt-TiO₂, respectively. Consequently Ru was selected.

On the basis of the computational high-throughput screening on 256 pure metals and alloys established by Nørskov and co-workers [17], four Ru-based bimetallic alloys were selected: RuCu, RuPd, RuAg and RuPt. These four bimetallic combinations should yield materials predicted by the calculations to have activities comparable to, or even better than, pure Ru for the hydrogen evolution reaction [17].



Fig. 2. Volume of hydrogen generated as a function of time: Ru-TiO $_2$ vs. Pt-TiO $_2$.



Fig. 3. Volume of hydrogen generated as a function of time for the Ru-based bimetallic alloys.

For bimetallic alloys, segregation may occur. Segregation is the phenomenon by which one metal segregates to the surface of another metal and this controls then the surface composition of alloys. Nørskov and co-workers [18] have compiled the calculated surface segregation energies in transition-metal alloys. According to these data, Cu, Pd, Ag and Pt should segregate when they alloy to Ru; in other words, the surface of the alloys RuCu, RuPd, RuAg and RuPt should be enriched with Cu, Pd, Ag and Pt, respectively; the Ru aggregates at the alloy surface should be smaller and better dispersed than for a surface of pure Ru but, likely, their number should be lower.

Fig. 3 plots generated volume of hydrogen as a function of time for the Ru-based bimetallic alloys. Their activity decreases in the order Ru>RuPt>RuPd>RuAg>RuCu, with HGRs of 38.8, 25.0, 14.9, 9.6 and $7.8 \text{ mL}(\text{H}_2) \text{ min}^{-1}$, respectively. Note that Ag-TiO₂, Cu-TiO₂ and Pd-TiO₂ were rather inactive with HGRs of 0.02, 0.04 and 0.3 mL(H₂) min⁻¹, respectively. The addition of a metal to Ru does not improve the reactivity of Ru. PtAg-TiO₂ was also prepared and compared to Pt-TiO₂, the former being less competitive than the latter: HGRs of 6.4 and 9.1 mL(H₂) min⁻¹, respectively. Krishnan et al. [14] have reported PtRu > Ru > Pt (all supported over $LiCoO_2$) but no explanation about the synergetic effect of Pt and Ru is given. An electronic effect (variation in the d-band centre of the metals and so in the metals electronic structure) and/or a geometric effect (segregation occurrence and heterogeneity in the composition of the alloy surface) might justify the best activity of this bimetallic alloy. In the present study, such synergetic effect was not observed (Fig. 3), and therefore, alloying Ru is ineffective. The predictions from ref. [17] are unfortunately not confirmed by our experiments. Hydrogen generation by NaBH₄ hydrolysis may be more complicated than the hydrogen evolution reaction because of the presence of adsorbed boron-based compounds (Fig. 1). Aside from that it seems that the reactivity of the Ru-based bimetallic alloys is closely linked to that of Ru (Fig. 3). From this observation, Ru_xPt_y-TiO₂ catalysts, for which the atomic ratios x:y were varied (1:0, 2:1, 1:1, 1:2, 0:1), were prepared. Fig. 4 shows their reactivity. The larger the

proportion of Ru in the alloy is, the more active Ru_xPt_y -TiO₂ is. Because of the occurrence of segregation for each of the Ru-based bimetallic alloys [18], RuCu, RuPd and RuAg are less active than pure Ru because the surface of the alloy is very likely enriched with the inactive metal (i.e., Cu, Pd and Ag); hence, the observed activity is that of Ru, which is present at the surface of the alloy in lower concentrations than for pure Ru. Regarding RuPt, its activity is better than those of the three other alloys because Pt is an active metal that likely participate to the reaction even if the global activity is lower than that of pure Ru. Similarly, Liu et al. [11] have remarked that Raney Ni₂₅Co₇₅ > Raney Ni₅₀Co₅₀ > Raney Ni₇₅Co₇₅ while Raney Co > Raney Ni; the reactivity of the Raney alloy seems to depend more on the content of the most active metal, i.e., Co. A last observation from Fig. 4 is that Ru-TiO₂ and Ru₂Pt₁-TiO₂ showed similar activities; it was also the case for Ru₁Pt₁-TiO₂ and Ru₁Pt₂-TiO₂. This observation may suggest that the content of active sites at the surface of these pairs of catalysts would be alike.

To summary, the activity of the different catalysts decreases in the order $Ru \sim Ru_2Pt_1 > RuPt \sim Ru_1Pt_2 > RuPd > RuAg \sim Pt > RuCu > PtAg$. Alloying Ru with an inactive metal like Cu, Pd and Ag is uninteresting since Ru-TiO₂ is more active than the bimetallic catalysts. New tracks of investigations remain to explore. The reactivity of Ru might improve if impurities (a few percent of metal) are added [19]. Such study, in which Ru is "doped", is in progress.

3.3. Durability of Ru₂Pt₁-TiO₂

Catalyst durability is crucial for NaBH₄-based hydrogen application. In accordance with the procedure reported by Ye and co-workers [20,21], used Ru₂Pt₁-TiO₂ was separated from the NaBH₄ solution, washed seven times with deionised water, dried (at 120 °C for 12 h) and re-used. Fig. 5 shows the cycle behaviour on hydrogen generation activity for Ru₂Pt₁-TiO₂. There was no noteworthy decrease in the catalytic activity. The HGRs were similar: 37.9, 36.7 and 37.1 mL(H₂) min⁻¹ for cycles 1, 3 and 5, respectively. As it was the case for Ye and co-workers [21],



Fig. 4. Volume of hydrogen generated as a function of time for the Ru_xPt_y -TiO₂ catalysts (atomic ratio *x*:*y* = 1:0, 2:1, 1:1, 1:2, 0:1).



Fig. 5. Multi-cycle operations of 1 wt.% Ru₂Pt₁-SZ.

the precipitation of NaB(OH)₄, a by-product of the hydrolysis reaction, was not observed. The durability is a major criterion for a catalyst and the results show that Ru_2Pt_1 -TiO₂ had good stability to hydrolysis of stabilised NaBH₄ solution.

Table 1 Hydrogen generation rates (HGRs) reported in the open literature

3.4. Achievable power levels

Amendola et al. [5] have estimated achievable power levels for their Ru-catalysed hydrogen generator. According to their assumptions and calculations, the same estimation is done in the present section.

Before that, it is necessary to report some HGRs (Table 1) that have been published in the open literature [5,10-12,14,15,20-24]. The 1.5 wt.% Pt-LiCoO₂ catalyst is outstanding with a HGR of $3.1 L(H_2) min^{-1} g^{-1}$ (catalyst) or 206.5 L(H₂) min⁻¹ g⁻¹(Pt) [12]. Except 10 wt.% PtRu-LiCoO₂ [14] and Ru [23], the other catalysts have HGRs below $1 L(H_2) min^{-1} g^{-1}$ (catalyst). Our Ru₂Pt₁-TiO₂ catalyst is among this latter group of catalysts but, when the HGRs in L(H₂) min⁻¹ g⁻¹(metal) are considered, Ru₂Pt₁-TiO₂ is the second best catalyst.

From the HGRs in Table 1, the achievable power levels (P) for each catalyst can be calculated [5]. It is assumed that 100% stoichiometric yield of hydrogen is achieved and that a polymer electrolyte membrane fuel cell operates at 0.7 V. Table 2 shows these data. Since P is proportional to HGR (despite small vari-

Catalyst	NaBH ₄ (wt.%); NaOH (wt.%)	Temperature (°C)	HGR ^a in $L(H_2) \min^{-1} g^{-1}$ (catalyst)	HGR ^a in $L(H_2) \min^{-1} g^{-1}$ (metal)	Reference
5 wt.% Ru dispersed on anionic resin	20; 10	25	0.2	4.1	[5]
Filamentary Ni mixed Co	12.5; (0.01 M)	Room temperature	0.1	0.1	[10]
Raney Ni ₅₀ -Co ₅₀	1; 10	20	0.7	0.7	[11]
1.5 wt.% Pt-LiCoO2	20; 10	22	3.1	206.5	[12]
10 wt.% PtRu-LiCoO2	5; 5	25	1.2	12.4	[14]
PtPd-carbon nanotubes	(0.03 M); (pH 13)	29	0.2	9.0	[15]
9 wt.% Co-γAl ₂ O ₃	1; 5	30	0.1	1.0	[20]
2 wt.% Pt-C	5; 5	30	0.2	8.5	[21]
Ni _x B	1.5; 20	40	0.3	0.3	[22]
Co-B	20; 5	20	0.9	0.9	[23]
Ru	20; 5	20	1.6	1.6	[23]
5 wt.% Ru-C	0.993; 3.75	25	0.7	12.9	[24]
$1 \text{ wt.}\% \text{ Ru}_2\text{Pt}_1\text{-TiO}_2$	2;4	20	0.15	15.2	Present study

^a Approximate values.

Table 2

Achievable power levels (*P*) for the catalysts given in Table 1

Catalyst	$P^{a,b}$ in W g ⁻¹ (catalyst)	$P^{a,b}$ in W g ⁻¹ (metal)	Reference	
5 wt.% Ru dispersed on anionic resin	18	370	[5]	
Filamentary Ni mixed Co	9	9	[10]	
Raney Ni ₅₀ -Co ₅₀	66	66	[11]	
1.5 wt.% Pt-LiCoO ₂	290	19130	[12]	
10 wt.% PtRu-LiCoO2	109	1126	[14]	
PtPd-carbon nanotubes	18	793	[15]	
9 wt.% Co-γAl ₂ O ₃	9	87	[20]	
2 wt.% Pt-C	18	743	[21]	
Ni _x B	24	24	[22]	
Co-B	84	84	[23]	
Ru	150	150	[23]	
5 wt.% Ru-C	64	1170	[24]	
1 wt.% Ru ₂ Pt ₁ -TiO ₂	14	1426	Present study	

^a $P = [I (26.8 \text{ A}) \times V (0.7 \text{ V}) \times M_{W}^{H_2} (2 \text{ g mol}^{-1}) \times \text{HGR} (L(H_2) \text{min}^{-1} \text{ g}^{-1}(\text{catalyst}) \text{ or } L(H_2) \text{min}^{-1} \text{ g}^{-1}(\text{metal}))]/[V_m (L \text{ mol}^{-1})]; \text{ adapted from reference [5].}$ ^b Approximate values.

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ations of $V_{\rm m}(T)$ with temperature (20–40 °C)), the comments in the previous paragraph are also valid here.

To summary, the catalytic abilities of Ru_2Pt_1 -TiO₂ in hydrogen generation are in the range of the highest values reported so far in the literature. Improvement ways exist, e.g., higher metal loading, doping of Ru with 'impurities' [19] and optimisation of the catalyst preparation. Such studies are in progress.

4. Conclusion

Hydrogen generation by hydrolysis of NaBH₄ was studied using Ru- and Pt-based bimetallic alloys, which were supported over titanium oxide TiO₂. The activity of the investigated catalysts decreased in the order Ru~Ru₂Pt₁ > RuPt~Ru₁Pt₂ > RuPd > RuAg~Pt > RuCu > PtAg. Alloying Ru with an inactive metal like Cu, Pd and Ag was ineffective because Ru-TiO₂ was more active than the bimetallic catalysts.

The catalytic abilities of Ru_2Pt_1 -TiO₂ in hydrogen generation are in the range of the highest values reported so far in the literature with a hydrogen generation rate of 15.2 L(H₂)min⁻¹ g⁻¹(RuPt). Durability test was performed for this catalyst. Used Ru₂Pt₁-TiO₂ was separated from the NaBH₄ solution, washed with deionised water, dried and reevaluated: almost the same catalytic activities as fresh catalyst were obtained during several cycles. The Ru₂Pt₁-TiO₂ catalyst showed quick response and good durability. These results are rather promising and improvement ways exist (e.g., optimisation of the metal(s) loading or doping of the active metal).

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