

# Kinetics of Ru-promoted sulphated zirconia catalysed hydrogen generation by hydrolysis of sodium tetrahydroborate

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## Abstract

Pure hydrogen can be catalytically generated by hydrolysis of sodium tetrahydroborate  $\text{NaBH}_4$ . The present paper reports the kinetics of hydrolysis of aqueous alkaline solution of  $\text{NaBH}_4$ . The investigated catalyst was 1 wt% Ru-promoted sulphated zirconia. The reaction orders for both  $\text{NaBH}_4$  and  $\text{NaOH}$ , the reaction order for Ru and the apparent activation energy were determined. The hydrogen generation rate can be written following a power law:  $r = k[\text{NaBH}_4]^{0.23}[\text{NaOH}]^{-0.35}[\text{Ru}]^{1.27}$ . The activation energy for the hydrogen generation reaction is of  $76 \text{ kJ mol}^{-1}$ . Otherwise, the present paper shortly reviews the kinetic data that are available in the open literature and notices the discrepancies that exist for these data. The kinetic data of the present study also contribute to these discrepancies.

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**Keywords:** Hydrogen; Kinetics; Ru-promoted sulphated zirconia; Sodium tetrahydroborate

## 1. Introduction

Prof. Herbert C. Brown (1912–2004) won the Nobel Prize in Chemistry 1979 [1] “for the development of the use of boron-containing compounds, into important reagents in organic synthesis” [2] as well as the inventor (with the late Prof. H.I. Schlesinger) of sodium tetrahydroborate  $\text{NaBH}_4$  [3]. Although rather overlooked in recent years, this chemical has been known as a viable hydrogen generator since the 1950s [3].

Hydrogen is an energy carrier that has a great potential as an environmentally clean energy fuel. It has the highest energy content of any common fuel by weight (about three times more than gasoline), but the lowest energy content by volume (about four times less than gasoline) [4]. This presents great transportation and storage hurdles. Storage systems being developed include compressed hydrogen, liquid hydrogen, adsorption on solids of large surface area, metal hydrides, and light hydrides [5].  $\text{NaBH}_4$  is a light solid hydride (or chemical hydride) [6]. It increasingly interests because its hydrogen content is of 10.7 wt%. An aqueous alkaline solution of  $\text{NaBH}_4$  is non-flammable and stable

and provides a safe method of hydrogen storage/transport [7]. The basic hydrogen reaction producing reaction (hydrolysis) is  $\text{NaBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{NaB}(\text{OH})_4 + 4 \text{H}_2 + \text{heat}$  ( $-300 \text{ kJ mol}^{-1}$ ). The hydrolysis reaction is controllable since the hydrogen generation only occurs in the presence of catalyst [7]. Generating hydrogen catalytically from  $\text{NaBH}_4$  solution has several advantages [7], e.g., generated hydrogen is high purity (no CS, no S) and humidified; hydrogen can be generated even at  $0^\circ\text{C}$ ; the reaction products,  $\text{H}_2\text{O}$  and  $\text{NaB}(\text{OH})_4$ , are environmentally safe; and,  $\text{NaB}(\text{OH})_4$  can be recycled. The main problem of  $\text{NaBH}_4$  is its cost and the main research activity in this area is in the development of alternative processes for regenerating  $\text{NaBH}_4$  from dehydrated  $\text{NaB}(\text{OH})_4$  that is  $\text{NaBO}_2$  [8].

Catalysts are essential and the catalysts used are transition metal-based: metal salts [9]; metal borides [10]; La- and Ni-based intermetallic compounds ( $\text{LaNi}_{4.5}\text{M}_{0.5}$ , M: metal) [11]; fluorinated metals [12]; bulk metals [13]; Raney metals [14]; and metal-promoted metal oxides [15]. In the course of examining the interaction of  $\text{NaBH}_4$  with heavy metals, Prof. H.C. Brown and his namesake and collaborator C.A. Brown [9] observed that many of these exerted a powerful catalytic effect on the  $\text{NaBH}_4$  hydrolysis; the Pt family were effective:  $\text{Ru, Rh} > \text{Pt} > \text{Co} > \text{Ni} > \text{Os} > \text{Ir} > \text{Fe} \gg \text{Pd}$ . Besides the authors noticed that  $\text{NaBH}_4$  reduced these metals to the elementary state, in a form, which exhibited high-catalytic activity for hydrolysis.

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### Nomenclature

$A$	pre-exponential factor
$E_a$	activation energy ( $\text{J mol}^{-1}$ )
$k$	rate constant
$[\text{NaBH}_4]$	molar concentration of $\text{NaBH}_4$
$[\text{NaOH}]$	molar concentration of $\text{NaOH}$
$r$	HGR ( $\text{mol}(\text{H}_2)\text{L}^{-1}$ )
$R$	gas constant, $8.31451\text{ J K}^{-1}\text{ mol}^{-1}$
$[\text{Ru}]$	molar concentration of $\text{Ru}$
$T$	temperature (K)

### Greek symbols

$\alpha$	reaction order with respect to $\text{NaBH}_4$
$\beta$	reaction order with respect to $\text{NaOH}$
$\chi$	reaction order with respect to $\text{Ru}$

On the basis of this study,  $\text{Ru}$  was selected to be the active metal of the catalyst of the present study.

Guella et al. [16] justly wrote that the state of knowledge was depleted for metal-catalysed  $\text{NaBH}_4$  hydrolysis. As for Zhang et al. [17], they commented that kinetic studies were rather limited. Kinetics studies are essential because they can provide information concerning the reactant(s) role and the catalyst behaviour. In this study, kinetics of catalytic hydrolysis of aqueous alkaline solution of  $\text{NaBH}_4$  was studied over a novel catalyst, 1 wt%  $\text{Ru}$ -promoted sulphated zirconia.

## 2. Experimental

### 2.1. Catalyst

Sulphated zirconia  $\text{ZrO}_2\text{-SO}_4^{2-}$  (SZ) was prepared according to a one-step sol-gel method [18]. An *n*-propyl alcohol (Aldrich) solution of 10 wt% zirconium *n*-propoxide (Aldrich) and an aqueous solution of sulphuric acid (Aldrich) were distinctly prepared. The amount of sulphuric acid was determined in order to have 5 wt% of sulphur in the catalyst prior the calcination stage. The solution of sulphuric acid was added to the solution of zirconium *n*-propoxide under vigorous stirring. A gel formed. The gel was stirred for 2 h and was dried at  $80^\circ\text{C}$  for 18 h. The solid was then calcined at  $625^\circ\text{C}$  for 4 h. As prepared, SZ had a specific surface area of  $88\text{ m}^2\text{ g}^{-1}$  and final sulphur content (after calcination) of 1.31 wt% and it showed a tetragonal crystalline phase (unpublished results), what is in accordance with to data already reported [18,19]. The impregnation of  $\text{Ru}$  onto SZ was as follows. The desired amount of  $\text{Ru}$  (0.5, 1, 2, 3 or 4 wt%) was added from an aqueous solution of  $\text{RuCl}_3$  (Strem). The mixture was stirred for 1 h and was dried in an oven for 12 h. The catalyst is denoted  $\text{Ru-SZ}$ .

### 2.2. Apparatus

In typical hydrogen generation experiments (apparatus adapted from Ref. [20]), 20 mL of an aqueous alkaline ( $\text{NaOH}$ ,

1 M, Aldrich) solution of  $\text{NaBH}_4$  (Aldrich) filled a sealed flask. The sealed flask was fitted with an outlet tube for collecting evolved hydrogen. The temperature  $T$  was varied and then maintained thanks to a water bath.  $\text{Ru-SZ}$  was added to the solution under stirring (not to have external diffusion effects, 400 rpm). 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 initial hydrogen generation rate (HGR) was calculated in the time range 1–5 min. The relative error on the measured volume was of about 2%.

### 2.3. Kinetic study

In such a way to get a maximum of information, the experiments were performed as follows. All kinetic data were measured using fresh  $\text{Ru-SZ}$ . Studies were carried out over a  $\text{NaBH}_4$  concentration range from 0.132 to 0.661 M and a  $\text{NaOH}$  concentration range from 0.1 to 1.3 M. The amount of catalyst was varied from 0.05 to 0.45 g. Besides, the  $\text{Ru}$  loading was varied from 0.5 to 4 wt%. HGRs were measured at a low-temperature range of 281–297 K, where thermal hydrolysis of stabilised  $\text{NaBH}_4$  solutions is approximately zero [17]. Initial HGRs were measured. Theoretically the maximum HGR occurs at the beginning of the reaction since the concentration of the reactant  $\text{NaBH}_4$  is the highest and the concentration of the by-product  $\text{NaB}(\text{OH})_4$  is the lowest. Note that the production of  $\text{NaB}(\text{OH})_4$  is detrimental to the HGR. For instance, Shang and Chen [21] showed that, when  $\text{NaB}(\text{OH})_4$  was saturated in the solution, the HGR significantly decreased, most probably due to its blockage of the catalytic sites. Hence, the HGRs were measured during the initial 5 min of hydrolysis.

## 3. Results and discussion

### 3.1. Preliminaries

$\text{NaBH}_4$  self-hydrolyses (in the absence of a catalyst) in aqueous solution but it can be stabilised by addition of  $\text{NaOH}$ . Under our selected experimental conditions, the HGR was of  $<0.01\text{ mL h}^{-1}$  ( $<0.2\text{ }\mu\text{L min}^{-1}$ ), what is negligible. Hydrogen generation with SZ was assessed and, in our selected experimental conditions, it was of  $0.04\text{ mL h}^{-1}$  ( $0.7\text{ }\mu\text{L min}^{-1}$ ). SZ can be regarded as being inactive. In all the experiments of the present study, the hydrogen generation started immediately without any induction time, as was the case with Guella et al. [16], Mitov et al. [22] and Özkaz and co-worker [23].

Zhang et al. [17] studied the kinetics of hydrolysis of stabilised  $\text{NaBH}_4$  solutions for a Ni-metal supported catalyst and represented the HGR by the expression  $r = k[\text{NaBH}_4]^{-0.41}[\text{NaOH}]^{0.13}[\text{H}_2\text{O}]^{0.68}$ . The reaction order for  $\text{H}_2\text{O}$  was determined from the variations of  $\text{H}_2\text{O}$  concentration during the course of an experiment but was checked for several experiments. This order of 0.68 showed the importance of water management for effective  $\text{NaBH}_4$  hydrolysis since water is the key reactant for hydrogen generation and the key solvent for the by-product  $\text{NaB}(\text{OH})_4$ . The authors did not investigate the effect

Table 1  
Hydrogen generation rates (in bold the varying parameters)

Temperature (°C)	Ru–SZ weight (mg)	Ru loading (wt%)	[NaBH <sub>4</sub> ] (M)	[NaOH] (M)	$r$ (10 <sup>-4</sup> mol(H <sub>2</sub> )L <sup>-1</sup> )
24	250	1	<b>0.132</b>	1	6.3
24	250	1	<b>0.264</b>	1	7.3
24	250	1	<b>0.397</b>	1	8.4
24	250	1	<b>0.529</b>	1	8.5
24	250	1	<b>0.661</b>	1	9.1
24	250	1	0.529	<b>0.1</b>	19.6
24	250	1	0.529	<b>0.4</b>	12.8
24	250	1	0.529	<b>0.7</b>	10.8
24	250	1	0.529	<b>1</b>	8.5
24	250	1	0.529	<b>1.3</b>	8.1
24	<b>50</b>	1	0.529	1	1.0
24	<b>150</b>	1	0.529	1	5.4
24	<b>250</b>	1	0.529	1	8.5
24	<b>350</b>	1	0.529	1	13.7
24	<b>450</b>	1	0.529	1	16.9
24	250	<b>0.5</b>	0.529	1	2.5
24	250	<b>1</b>	0.529	1	8.5
24	250	<b>2</b>	0.529	1	17.6
24	250	<b>3</b>	0.529	1	30.0
24	250	<b>4</b>	0.529	1	37.4
<b>8</b>	250	1	0.529	1	1.6
<b>11</b>	250	1	0.529	1	2.2
<b>15</b>	250	1	0.529	1	3.6
<b>19</b>	250	1	0.529	1	6.5
<b>24</b>	250	1	0.529	1	8.5

of the catalyst concentration on the HGR. In the present study, the reaction order for H<sub>2</sub>O was not determined because, in our selected experimental conditions, the variation of the concentration of H<sub>2</sub>O during the time range 1–5 min was found as being nil (by calculations). In fact, in our experimental conditions, the molar ratio [H<sub>2</sub>O]/[NaBH<sub>4</sub>] was of ~100.

In the present study, the HGR is given following a power law  $r = k[\text{NaBH}_4]^\alpha[\text{NaOH}]^\beta[\text{Ru}]^x$  where  $k = A \exp(-E_a/RT)$ . Table 1 shows all the HGRs that were obtained and used to determine the orders and the apparent activation energy.

### 3.2. Reaction order for NaBH<sub>4</sub>

In the existing literature, the reaction order with respect to NaBH<sub>4</sub> was obtained in two ways. A first group of researchers determined the order from variation of HGR with time in the course of an experiment. Often, the volume of hydrogen increased linearly with time, implying then zero-order kinetics [14,20,22–28]. Hence, Amendola et al. [20] proposed that the first-step involved a surface reaction, most likely BH<sub>4</sub><sup>-</sup> adsorption on Ru. For Kojima et al. [25], an order of 0 indicated that HGR was controlled by the catalyst (1.5 wt% Pt–LiCoO<sub>2</sub>). A second group of researchers determined the order for NaBH<sub>4</sub> from variation of the initial concentration of NaBH<sub>4</sub>. There was a discrepancy between the orders found. Negative orders were reported by Zhang et al. [17] (–0.41 with Ni-supported catalyst) or were implied by Mitov et al. [22] (CoMnB on Ni foam) and Ye et al. [27] (9 wt% Co–γAl<sub>2</sub>O<sub>3</sub>). The latter authors explained their observation by an increase in solution viscosity as first suggested by Amendola et al. [20]. A zero-order was reported by Özkar and

co-worker [29]. Positive orders, i.e., first-order, were reported by Shang and Chen [21] (3 wt% Ru–C) and Peña-Alonso et al. [30] (PtPd–carbon nanotubes).

Fig. 1 shows the plot of the data in Table 1 (lines 1–5), which slope provides an estimate of the reaction order for NaBH<sub>4</sub>, found as being of 0.23. With 1 wt% Ru–SZ, an increase of the initial concentration of NaBH<sub>4</sub> has a positive effect on the HGRs as was the case with Shang and Chen 3 wt% Ru–C [21]. In our selected experimental conditions, the molar ratio [H<sub>2</sub>O]/[NaBH<sub>4</sub>] was of ~100; it was probably not optimum and therefore an increase of the NaBH<sub>4</sub> concentration improved the HGR. The first group of researchers discussed above determined the reaction order for NaBH<sub>4</sub> from the plot ‘volume of hydrogen generated versus time’. Fig. 2 shows such

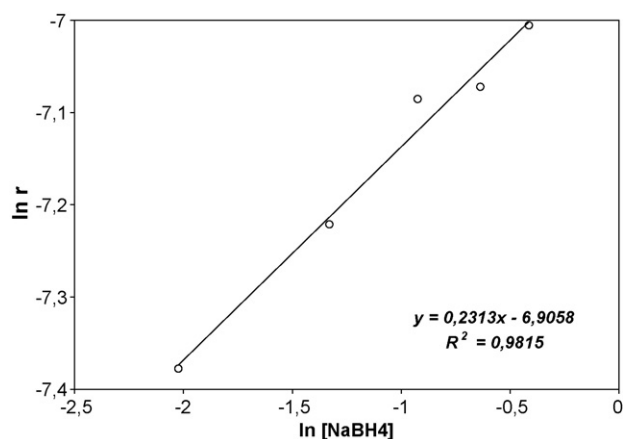


Fig. 1. Determination of the reaction order with respect to NaBH<sub>4</sub>.

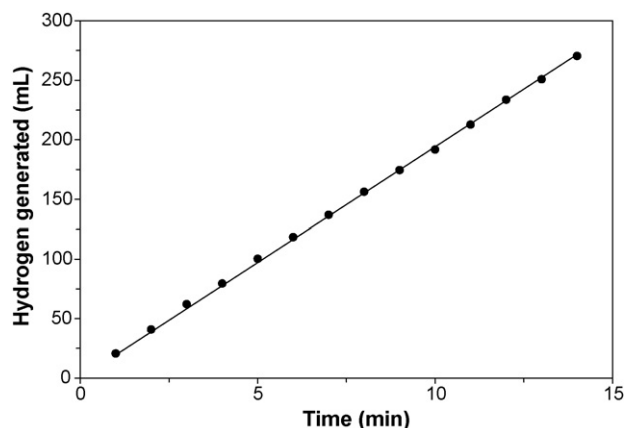


Fig. 2. Volume of hydrogen generated as a function of time for 1 wt% Ru-SZ (250 mg; 24 °C; [NaBH<sub>4</sub>] = 0.529 M; [NaOH] = 1 M).

a plot, which was monitored for the conversion of NaBH<sub>4</sub> over 1 wt% Ru-SZ. The volume of hydrogen increases linearly with time and this observation suggests an order of zero for NaBH<sub>4</sub> [14,20,22–28]. All of the experiments reported in Table 1 showed the same result. Zhang et al. [17] emphasised that the zero-order kinetics contradicted observed HGR variations with increases in initial NaBH<sub>4</sub> concentrations. These contradictory orders are difficult to explain but it is important to note that the features of the reaction medium in the course of the hydrolysis experiment change with time (e.g., NaBO<sub>2</sub> production, variation of pH, change in viscosity and increase of the temperature) while the features of the reaction medium for experiments varying the initial concentration of NaBH<sub>4</sub> are identical. Zhang et al. [28] developed an interesting methodology for determining the kinetics of the hydrolysis reaction since they analysed their experimental data by regarding various kinetic models: namely zero-order kinetic, first-order kinetic, *n*th-order kinetic and Langmuir–Hinshelwood models. This latter model assumed that the reaction consisted of two important steps: the equilibrated adsorption of NaBH<sub>4</sub> on the surface of the catalyst and the reaction of the adsorbed species on the catalyst surface. This model successfully captured the zero-order reaction behaviour of the reaction. Our data, for example those in Fig. 2, were then analysed in this way. According to the information given by Zhang et al. [28], we tried the four models. The zero-order model, the *n*th-order model with *n* ~ 0–0.24 and the Langmuir–Hinshelwood model fitted our data well. This analysis confirmed the zero-order behaviour at 24 °C and as Kaufman and Sen [10] one may suggest pseudo-zero-order kinetics.

### 3.3. Reaction order for NaOH

Hua et al. [31] reported that, with the increase of the NaOH concentration from 0 to 20 wt%, the HGRs with Ni<sub>x</sub>B increased while the HGRs with 2 wt% Ru-C decreased, implying positive and negative orders with respect to NaOH, respectively. The authors admitted then that these contradictory results were difficult to explain. For Shang and Chen [21] (3 wt% Ru-C), the addition of NaOH slowed down the HGR (negative order). A positive order, i.e., 0.13, was reported by Zhang et al. [17]

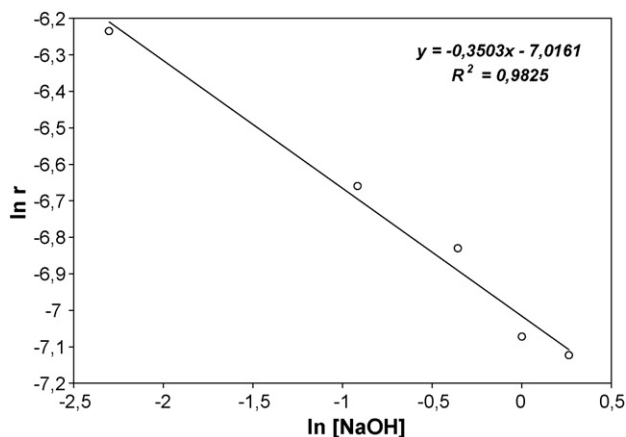


Fig. 3. Determination of the reaction order with respect to NaOH.

(Ni-supported catalyst), who remarked that it was not clear how NaOH affected rates but they surmised that NaOH might affect desorption of B(OH)<sub>4</sub><sup>-</sup> from the catalyst surface, thus affecting the active site renewal rate. Variations of the order for NaOH with the variation of NaOH concentration were observed by Jeong et al. [24] (CoB) and Ye et al. [27] (9 wt% Co-γAl<sub>2</sub>O<sub>3</sub>), i.e., increase of the HGR with the increase of the NaOH concentration from 1 to 10 wt% but decrease with further increase. For Ye et al. [27], the effect of NaOH concentration on the NaBH<sub>4</sub> hydrolysis was greatly dependent on the catalyst. As for Liu et al. [14], they ascribed a decrease in water activity to the drop of the HGR above 20 wt% of NaOH. In fact, it seems that the reaction order with respect to NaOH is greatly dependent on the selected experimental conditions as well as the catalysts.

Fig. 3 shows the plot of the data in Table 1 (lines 6–10), which slope provides an estimate of reaction order for NaOH, i.e., -0.35. A negative order was reported by Hua et al. [31] with 2 wt% Ru-C and Shang and Chen [21] with 3 wt% Ru-C. The effect of NaOH concentration on the NaBH<sub>4</sub> hydrolysis is likely dependent on the catalyst [27] and the increase of NaOH concentration might have negative effects on the Ru-based catalysts. Besides, an increase of the solution viscosity might be ascribed to this negative effect [20].

### 3.4. Reaction order for Ru

Guella et al. [16] investigated the kinetics of NaBH<sub>4</sub> hydrolysis for 10 wt% Pd-C by <sup>11</sup>B NMR measurements. With this catalyst, the hydrogen production showed a first-order kinetic dependence on Pd concentration. An order of one was also reported by Özkaz and co-workers [23,29] for Ru and Ni nanoclusters, respectively. Kojima et al. [25] reported the expression  $k = 0.0436 + 0.00917 \cdot c$ , with *c* the content of the Pt-LiCoO<sub>2</sub> catalyst. In fact, the few studies that report a reaction order for the catalyst report a positive order.

Fig. 4 shows the plot of the data in Table 1 (lines 11–15 and lines 16–20). The reaction order for the active component of the catalyst, i.e., Ru, was determined in two ways: variation of the weight of the Ru-SZ catalyst from 50 to 450 mg; for 250 mg of Ru-SZ, variation of the Ru loading from 0.5 to 4 wt%. The

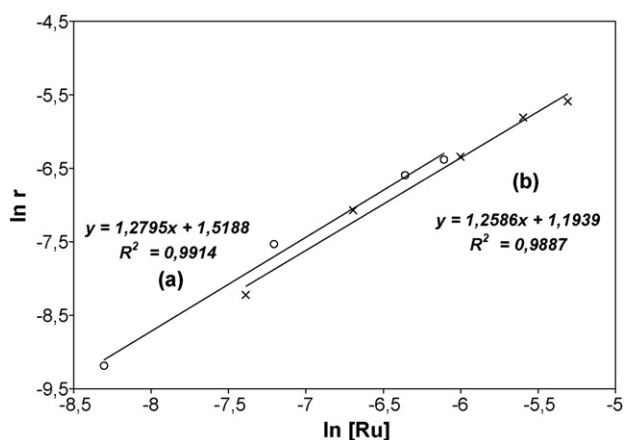


Fig. 4. Determination of the reaction order with respect to Ru: (a) from the variation of the weight of 1 wt% Ru–SZ and (b) from the variation of the Ru loading (wt%) for 250 mg of Ru–SZ.

orders are identical: namely 1.28 and 1.26, respectively; hence an order of 1.27 is retained. This suggests that the nature of the Ru active sites on the catalyst surface is unchanged with the increase of the Ru loading and that the increase of the Ru loading only affects the concentration of the Ru surface sites. A reaction order of 1.27 for Ru agrees with those reported in the literature [16,23,29].

### 3.5. Apparent activation energy

Fig. 5 shows the plot of the data in Table 1 (lines 21–25) that enables the determination of the apparent activation energy. Apparent activation energy of  $76 \text{ kJ mol}^{-1}$  is found. This value is higher than those reported through the open litera-

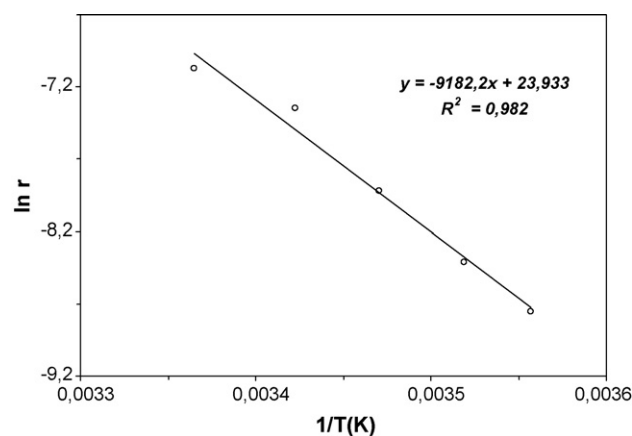


Fig. 5. Determination of the apparent activation energy.

ture for  $\text{NaBH}_4$  hydrolysis over transition metal-based catalysts [10,14,17,20–24,26–31]. Table 2 shows them. The values are scattered and disparate; they vary from 19 to  $75 \text{ kJ mol}^{-1}$ , most likely due to differences in the experimental conditions as well as in the intrinsic physical–chemical properties of the metals (geometric effect like, e.g., dispersion of the metal, metallic particles size and surface area; electronic effect induced by a support or a second metal). The 1 wt% Ru–SZ catalyst appears less active compared to all of these solid catalysts (Table 2) since increased activation energy suggests lower catalytic activity [17,31]. It shows apparent activation energy that is similar to that of Zhang et al. 3 wt% Ru–C [28]. Note that Özkar and co-workers reported two different values for the apparent activation energy obtained with Ru nanoclusters namely 29 [23] and  $41 \text{ kJ mol}^{-1}$  [26]. Ru nanoclusters were prepared following a procedure adapted from a method referenced by the authors and these data seems to have

Table 2  
Apparent activation energies reported through the open literature

Catalyst	$E_a$ ( $\text{kJ mol}^{-1}$ )	Experimental conditions for $E_a$ $\text{NaBH}_4$ – $\text{NaOH}$	References
Ni	71	$5.10^{-3} \text{ mol-0}$	[10]
Ni	63	1–10	[14]
Ni	73	$0.15 \text{ mol L}^{-1}\text{-0}$	[29]
Ni nanoclusters	54	$0.15 \text{ mol L}^{-1}\text{-0}$	[29]
Ni-supported	52	$5.53\text{-}0.79 \text{ mol L}^{-1}$	[17]
Raney Ni	63	$5.10^{-3} \text{ mol-0}$	[10]
Raney Ni	51	1–10	[14]
$\text{Ni}_x\text{B}$	38	1.6–10 in wt%	[31]
Raney Co	54	1–10	[14]
Co	75	$5.10^{-3} \text{ mol-0}$	[10]
Co	42	1–10	[14]
Raney $\text{Ni}_{50}\text{Co}_{50}$	53	1–10	[14]
9 wt% Co– $\gamma\text{Al}_2\text{O}_3$	33	5–5 in wt%	[27]
9 wt% Co–C	46	5–5 in wt%	[27]
CoB	65	20–5	[24]
CoMnB on Ni foam	55	5–5	[22]
Ru supported on anion exchange resin	47	20–10 in wt%	[20]
Ru nanoclusters	29	$0.15 \text{ mol L}^{-1}\text{-0}$	[23]
Ru nanoclusters	41	$0.15 \text{ mol L}^{-1}\text{-0}$	[26]
Ru nanoclusters	43	$0.15 \text{ mol L}^{-1}\text{-}10 \text{ wt\%}$	[26]
3 wt% Ru–C	37	$1.32 \text{ mol kg}^{-1}\text{-}5 \text{ wt\%}$	[21]
3 wt% Ru–C	69		[28]
PtPd–Carbon nanotubes	19	0.015 M–pH 13	[30]

been determined in identical experimental conditions. As this difference is quite important, one can deplore that the authors did not discuss that in Ref. [26]. These authors showed, besides, that NaOH did not affect the apparent activation energy: 41 and 43 kJ mol<sup>-1</sup> without NaOH and with NaOH, respectively [26].

### 3.6. Summary

The established HGR can be given following a power law, namely  $r = k[\text{NaBH}_4]^{0.23}[\text{NaOH}]^{-0.35}[\text{Ru}]^{1.27}$  with  $k = A \exp(-76.10^3/RT)$ .

It is besides interesting to compare the efficiency of our catalysts to that of other catalysts reported in the literature and a good “tool” is the HGR given in L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(catalyst) or in L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(Ru). In a previous paper, we have listed most of them [32]. Note that the best HGR ever published is 3.1 L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(catalyst) or 206.5 L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(Pt) for 1.5 wt% Pt–LiCoO<sub>2</sub> at 22 °C [15]: this catalyst is outstanding. In the present study, the best result was 0.36 L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(catalyst) or 9.1 L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(Ru) for 4 wt% Ru–SZ at 24 °C (Table 1, line 20) and this HGR is similar to those of most catalysts [32]. Indeed, our catalyst can be directly compared to two Ru-based catalysts. Amendola et al. [20] reported HGRs of 0.2 L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(catalyst) or 4.1 L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(Ru) for 5 wt% Ru dispersed on anionic resin at 25 °C (20 wt% NaBH<sub>4</sub>, 10 wt% NaOH); their experimental conditions are less favourable on account of the high concentration of NaOH. Zhang et al. [28] reported HGRs of 0.7 L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(catalyst) or 12.9 L(H<sub>2</sub>) min<sup>-1</sup> g<sup>-1</sup>(Ru) for 5 wt% Ru–C at 25 °C (1 wt% NaBH<sub>4</sub>, 4 wt% NaOH). These data suggest that the performances of these three Ru-based catalysts are quite similar even if the proportion of Ru in our catalyst 4 wt% Ru–SZ is smaller. Our HGR results are promising and improvement ways are going to be explored.

### 4. Conclusion

The kinetics of catalytic hydrolysis of aqueous alkaline solution of NaBH<sub>4</sub> was studied over 1 wt% Ru-promoted sulphated zirconia, in order to determine the reaction orders and the apparent activation energy. The established hydrogen generation rate is described following a power law and its expression is:  $r = k[\text{NaBH}_4]^{0.23}[\text{NaOH}]^{-0.35}[\text{Ru}]^{1.27}$ . The activation energy for the hydrogen generation reaction is 76 kJ mol<sup>-1</sup>.

A short survey of the kinetic studies available in the open literature shows the discrepancies that exist for the reaction orders and the apparent activation energy. Negative, zero and positive orders are reported for NaBH<sub>4</sub> and NaOH. The apparent activation energy values vary from 19 to 75 kJ mol<sup>-1</sup>. However,

concerning the reaction order for the catalyst, a few papers having determined this datum report a positive order. In fact, the kinetic studies are at their early stages and that explains the discrepancies in the kinetic data.

### References

- [1] Official web site of the Nobel foundation, <http://www.nobelprize.org>.
- [2] Prof. Herbert C. Brown's biography available, <http://www.chem.purdue.edu/hcbrown>.
- [3] H.I. Schlesinger, H.C. Brown, collaborators, J. Am. Chem. Soc. 75 (1953) (a) 186–190, (b) 199–204, (c) 205–209, (d) 215–129.
- [4] Web site of the Energy Information Administration, Official Energy Statistics from the U.S. Government, <http://www.eia.doe.gov>.
- [5] L. Schlapbach, A. Züttel, Nature 414 (2001) 353–358.
- [6] A. Züttel, A. Borgschulte, S.I. Orimo, Scripta Mater. 56 (2007) 823–828.
- [7] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder, Int. J. Hydrogen Energy 25 (2000) 969–975.
- [8] J.H. Wee, K.Y. Lee, S.H. Kim, Fuel Process Technol. 87 (2006) 811–819.
- [9] H.C. Brown, C.A. Brown, J. Am. Chem. Soc. 84 (1962) 1493–1494.
- [10] C.M. Kaufman, B. Sen, J. Chem. Soc., Dalton Trans. (1985) 307–313.
- [11] I.I. Korobov, N.G. Mozgina, L.N. Blinova, Kinet. Catal. 48 (1995) 380–384.
- [12] S. Suda, Y.M. Sun, B.H. Liu, Y. Zhou, S. Morimitsu, K. Arai, N. Tsukamoto, M. Uchida, Y. Candra, Z.P. Li, Appl. Phys. A 72 (2001) 209–212.
- [13] J.H. Kim, K.T. Kim, Y.M. Kang, H.S. Kim, M.S. Song, Y.J. Lee, P.S. Lee, J.Y. Lee, J. Alloys Compd. 379 (2004) 222–227.
- [14] B.H. Liu, Z.P. Li, S. Suda, J. Alloys Compd. 415 (2006) 288–293.
- [15] Y. Kojima, K.I. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, Int. J. Hydrogen Energy 27 (2002) 1029–1034.
- [16] G. Guella, C. Zanchetta, B. Patton, A. Miotello, J. Phys. Chem. B 110 (2006) 17024–17033.
- [17] Q. Zhang, Y. Wu, X. Sun, J. Ortega, Ind. Eng. Chem. Res. 46 (2007) 1120–1124.
- [18] H. Armendariz, B. Coq, D. Tichit, R. Dutartre, F. Figuéras, J. Catal. 173 (1998) 345–354.
- [19] U.B. Demirci, F. Garin, Catal. Lett. 76 (2002) 45–51.
- [20] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, J. Power Sources 85 (2000) 186–189.
- [21] Y. Shang, R. Chen, Energy Fuels 20 (2006) 2149–2154.
- [22] M. Mitov, R. Rashkov, N. Atanasov, J. Mater. Sci. 42 (2007) 3367–3372.
- [23] S. Özkar, M. Zahmakiran, J. Alloys Compd. 404–406 (2005) 728–731.
- [24] S.U. Jeong, R.K. Kim, E.A. Cho, H.J. Kim, S.W. Nam, I.H. Oh, S.A. Hong, S.H. Kim, J. Power Sources 144 (2005) 129–134.
- [25] Y. Kojima, K.I. Suzuki, Y. Kawai, J. Power Sources 155 (2006) 325–328.
- [26] M. Zahmakiran, S. Özkar, J. Mol. Catal. A 258 (2006) 95–103.
- [27] W. Ye, H. Zhang, D. Xu, L. Ma, B. Yi, J. Power Sources 164 (2007) 544–548.
- [28] J.S. Zhang, W.N. Delgass, T.S. Fisher, J.P. Gore, J. Power Sources 164 (2007) 772–781.
- [29] Ö. Metin, S. Özkar, Int. J. Hydrogen Energy 32 (2007) 1707.
- [30] R. Peña-Alonso, A. Sicurelli, E. Callone, G. Carturan, R. Raj, J. Power Sources 165 (2007) 315–323.
- [31] D. Hua, Y. Hanxi, A. Xinping, C. Chuansin, Int. J. Hydrogen Energy 28 (2003) 1095–1100.
- [32] U.B. Demirci, F. Garin, J. Alloys Compd. (2007), doi:10.1016/j.jallcom.2007.08.077.