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Hydrogen generation from hydrolysis of sodium borohydride using sulfonated porous carbon as reagent/catalyst

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ABSTRACT

The hydrolysis of sodium borohydride as a source of hydrogen gas is studied at different mole ratios of H+ to $NaBH_4$. The sulfonated porous carbon (SPC) is used as a source of hydrogen ion and catalyst. It is found that the sulfonated porous carbon exhibits high activity for the hydrolysis of $NaBH_4$ to generate hydrogen gas at room temperature in comparison to Amberlyst-15 and Nafion-NR50. The kinetic rate constant of hydrolysis reaction is calculated by measurement of the evolved hydrogen gas as a function of time. The kinetic rate constant of $NaBH_4$ hydrolysis is approximately increased 7.6 times at presence of SPC as a solid acid/catalyst versus blank hydrolysis reaction. The activation energy of sodium borohydride hydrolysis is obtained 1.24 $KJmol^{-1}$. The kinetic rate constant (k_{app}, s^{-1}) of hydrogen generation reaction increased from 0.023 to 0.626 with increasing of $H^+_{(SPC)}/NaBH_4$ from 0.25 to 1.50. The SPC activity with mole ratio of $H^+/NaBH_4=1$ show an efficiency of 91% at time 25s.

Keywords: Hydrogen generation, Sulfonated porous carbon, Sodium borohydride, Kinetic.

1. Introduction

It is known that hydrolysis of alkaline and alkaline earth metal hydrides and complex hydrides (NaH, $NaAlH_4$, $NaBH_4$, LiH, $LiAlH_4$, $LiBH_4$, CaH_2, $Ca(BH_4)_2$, MgH_2, $Mg(BH_4)_2$, KH, KBH_4) can be used to generate hydrogen [1-3]. Among these chemical, hydrides, sodium borohydride (NaBH4) offers the most promise for meeting the technical target of 6 wt% hydrogen capacity set by US Department of Energy (DOE) [4]. Safety, controllability, stability and ease of handling are the advantages of NaBH4 in generation of hydrogen. The hydrolysis reaction can be initiated at an ambient temperature and proceeds in an auto-thermal manner, indicating that no energy input is needed to sustain the reaction. By using catalysts, rapid hydrogen generation in response to demand can be achieved, and its rate could also be easily controlled. The by-product of the hydrolysis reaction of sodium borohydride, i.e. $NaBO_2$, is environmentally benign and can be recycled as the raw material for regeneration to $NaBH_4$ [5]. These distinct advantages of hydrogen generation from $NaBH_4$ hydrolysis reaction make it an attractive and promising on-board hydrogen generation method for portable PEM (Proton exchange membrane) fuel cells. The hydrolysis reaction of $NaBH_4$ at presence of various catalysts and acids for hydrogen production are studied in the recent years [6-16].

In recent years, heterogeneous solid acid have gained importance due to environmental and economic considerations. The replacement of environmental hazardous catalysts with solid acid is one of the innovative trends; and the preparation of cheap, recyclable and nontoxic strong solid acids is an attractive area in green chemistry. Traditional homogeneous acid such as H_2SO_4, HCl, H_3PO_4, CH_3COOH or HCOOH are toxic, corrosive and also hard to remove from the reaction medium.

Sulfonated porous carbon (SPC) [17-19] with a high surface area and high density of sulfonic acid (SO3H) is a promising alternative for the sulfuric catalyst. (i) It is insoluble in common organic solvents, causes low corrosion and shows environmental acceptability. (ii) The products could be easily separated from the reaction mixture and the SPC is recoverable without decreasing its activity. (iii) It can be successfully used instead of sulfuric acid as a catalyst [20-23].

Porous carbon materials and products based on them are diffuse in many actual scientific applications. They are used as fuel cells and capacitors. Porous carbon materials with high surface areas and well developed porosities have attracted substantial attention because they can fulfill most of the desirable properties required for a suitable catalyst support. The stability in aggressive media at elevated

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temperature, feasibility of control parameters of the porous structure surface area in a broad range, and the physicochemical properties are the major advantages of carbon materials [24-28].

In this study, we investigated the behavior of hydrogen generation from $NaBH_4$ solution by adding SPC catalyst.

2. Experimental

2.1. General experimental information

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Scanning electron microscopy images (SEM) were taken on SEM SERON TECHNOLOGY AIS-2100. X-ray diffraction patterns (XRD) were obtained on a Bruker D8 ADVANCE instrument. The specific surface area and mean pore diameter (dp) were calculated from adsorption isotherms of nitrogen at 77 K using the standard Brunauer-Emmett-Teller (BET) equation, and were obtained on a NOVA 2200, Quantachrome Corporation, Version. The elementary analysis was obtained from Vario EL III of Elementar Company.

2.2. Preparation of SPC

Pine wood powder was used as starting material in the preparation of porous carbon (PC) material. In a typical procedure, wood powder (10 g) was impregnated with $ZnCl_2$ by immersion in aqueous solution of HCl (1.0 M, 50 ml) containing $ZnCl_2$ (20 g) under mechanical agitation at 25 °C for 15 h. After that, the supernatant liquid was separated by filtration and the remaining solid was oven-dried at 80 °C for 24 h. Then, the $ZnCl_2$-impregnated wood powder was placed in a boat like small size ceramic container and heated gradually from room temperature to 500 °C. The heating gradient was not faster than 10 °C min⁻¹. The heating time at maximum heat (500 °C) treatment temperature was 1 h. Thereafter, the sample was washed by heating in the aqueous HCl solution (5 %, 100 ml) at 100 °C for 1 h. Then, the resulting solid was filtered and rinsed with warm distilled water (50 °C) to confirm that the wash solution is free of zinc ions. The resultant activated porous carbon material was finally dried at 80 °C in an oven for approximately 24 h. Then, the activated porous carbon material (5 g) was heated for 15 h in oleum (18-24 wt% SO_3, 100 ml) at 180 °C under N_2 in order to introduce SO_3H. After heating and then cooling to room temperature, distilled water (400 ml) was added to the mixture. The black precipitate was filtered and repeatedly washed with boiling distilled water until impurities such as sulfate ions were no longer detected in the wash water. The sample was finally dried overnight in an oven at 80 °C to afford the sulfonated acid catalyst [17-19].

2.3. Hydrogen generation

Sodium borohydride (Merck), $NaBH_4$, with a purity of 99% was used as received. It was kept in a nitrogen atmosphere in order to avoid hydrolysis with moisture. The hydrogen-generation experiments were as follows. In a three-vent balloon, solid sodium borohydride and SPC were introduced into the reactor. The amount of SPC was 0.106 g (equal to 0.5 mmole H^+) and the mole ratios of solid acid to $NaBH_4$ were at values of 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50. The reactor temperature was controlled at room temperature (25 °C). The reactor exhaust was connected to a water-filled inverted burette. Then, 4.0 ml double-distilled water with desired temperature was injected into the reactor in the absence of any stirring of reactant. All of the experiments were video-recorded and the volume of evolved H_2 was obtained from the pictures of video. Each experiment was carried out three times in order to ensure reproducibility of the results. The volume of generated H_2 was used to calculate the $NaBH_4$ conversion for each reaction.

3. Results and discussion

3.1. Characterization of SPC

The density of SO_3H group of SPC was determined on the basis of elemental analysis. Total acid density (SO_3H^+ COOH) and (SO_3H^+ COOH$^+$ OH) were obtained using standard acid-base back-titration with bases of different strength: $NaHCO_3$ and NaOH solutions, respectively [29]. The results revealed the amounts of SO_3H, COOH, and phenolic OH groups are 3.55, 0.15, and 1.02 mmol g⁻¹, respectively.

The X-ray diffraction pattern of sulfonated porous carbon exhibits two broad and weak peaks (2θ = 10-30°, 35-45°) attributed to amorphous carbon (Fig. 1) [17]. The SEM image of SPC (Fig. 2) reveals the morphology and structure of amorphous carbon that is in agreement with XRD pattern. The sample was gold coated prior to scanning. The BET results show a surface area of 1260 m² g⁻¹ for prepared the SPC.

3.2. Hydrogen generation catalyzed by SPC

Sulfonated porous carbon (SPC) with SO_3H groups used as a heterogeneous solid acid in H_2 production from hydrolysis reaction of sodium borohydride. In acidic solutions, the hydrolysis of $NaBH_4$ proceeds as follows [30]:

$$BH_4^- + H^+ + 3H_2O \rightarrow B(OH)_3 + 4H_2 \qquad (1)$$
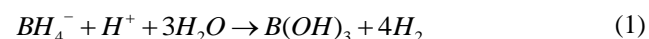
In Fig. 3, the volume of generated hydrogen gas at various mole ratios of $H^+_{(SPC)}/NaBH_4$ (0.25-1.50) at room temperature (25 °C) was shown within 120 s. As seen, the rate of hydrogen generation is increased with increasing of mole ratio of $H^+_{(SPC)}/NaBH_4$. The yield of more than 90% is obtained at mole ratio ≥ 1. But, the conversion of 40-80% of $NaBH_4$ is seen at mole ratios of smaller than 1 because the reaction is limited by the amount of $H^+_{(SPC)}$ ions. However, in mole ratio below 1, the generated H_2 volume is more than the expected volume based on stoichiometry of the reaction (Eq. 1). At mole ratio < 1.0, the rate of H_2 evolution shows two steps in hydrolysis reaction at presence SPC. In the first step, the H_2 evolution is obtained with high rate that show
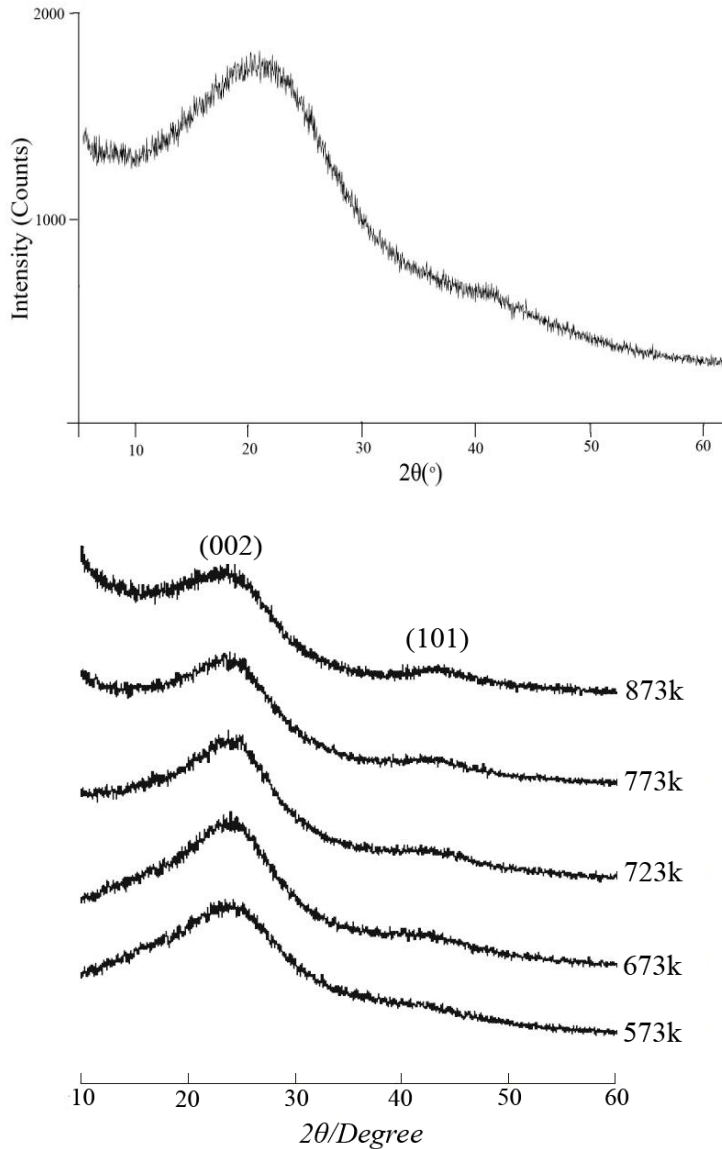
$$r = -\frac{d[NaBH_4]}{dt} = k[NaBH_4]^x [H^+]^y [H_2O]^z \qquad (2)$$

The powers of x, y and z are the reaction orders versus $NaBH_4$ concentration, $H^+_{(SPC)}$ concentration and water, respectively. It is noticed that: i) the concentration of water was considered as constant concentration due to the excess of water in the reactions, ii) the hydrogen ion concentration of SPC was 4.72 mmol g^{-1} and is a constant amount (0.106 g of SPC is equivalent 0.5 mmol H$^+$). This amount of SPC produces only 6.1 ml of hydrogen; hence, the first 6.1 ml of hydrogen was not taken into account in the calculations. According to the conditions, the Eq. (2) can be simplified as:

$$r = -\frac{d[NaBH_4]}{dt} = k'[NaBH_4]^x \qquad (3)$$

The reaction order versus the $NaBH_4$ concentration was determined in the course of experiment by using the xth order kinetics. With respect to $NaBH_4$ hydrolysis reaction, the pseudo-first order kinetic was applied for all the experiments. The regression coefficients R are obtained 0.970-0.993 (Fig. 4), which suggested that the reaction of hydrogen generation fitted well with the pseudo-first order kinetic model. The obtained kinetic rate constants and the half-time of the reaction at different ratios of $H^+_{(SPC)}/NaBH_4$ are collected in Table 1. The SPC did not show any effective on the $NaBH_4$ hydrolysis reaction at mole ratio of $H^+_{(SPC)}/NaBH_4$ of 0.25. This result, also, was observed obviously at mole ratios of 0.5 and 0.75 (Fig. 3). The spontaneous hydrolysis of $NaBH_4$ in the absence of any H^+ in the medium occurred as:

$$BH_4^- + 4H_2O \rightarrow B(OH)_4 + 4H_2 \qquad (4)$$

The kinetic equation of spontaneous hydrolysis of $NaBH_4$ is as follows:

$$r = -\frac{d[NaBH_4]}{dt} = k[NaBH_4]^x [H_2O]^y \qquad (5)$$

Fig. 1. (a) The X-ray diffraction patterns of the synthesized SPC, (b) The X-ray diffraction patterns of reference [17] at various carbonization temperatures.

hydrolysis reaction of $NaBH_4$ is catalyzed by SPC reagent. While, in the second step, the $NaBH_4$ hydrolysis is a non-catalyzed reaction or a spontaneous reaction and the H_2 evolution reaction is progressed with less rates. However, the hydrogen evolution occurs in one step in mole ratios ≥ 1 that show the hydrolysis of $NaBH_4$ is catalyzed by SPC.

3.3. Kinetic of hydrogen generation

The first part of hydrogen evolution curve (Fig. 3) in amplitude of 1-5 s was used to determine the kinetic rate constant of the hydrolysis reaction of $NaBH_4$ with SPC at different mole ratios. With respect to the hydrolysis reaction (Eq. 1), the following equation was used to show the equation of $NaBH_4$ hydrolysis with SPC as a solid acid.
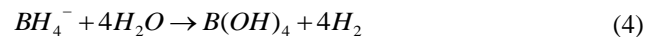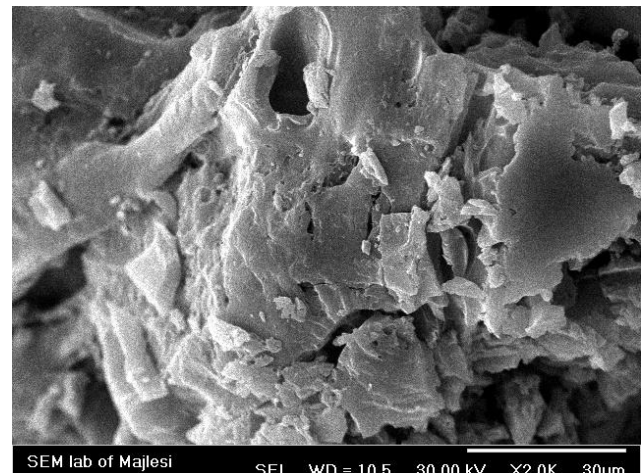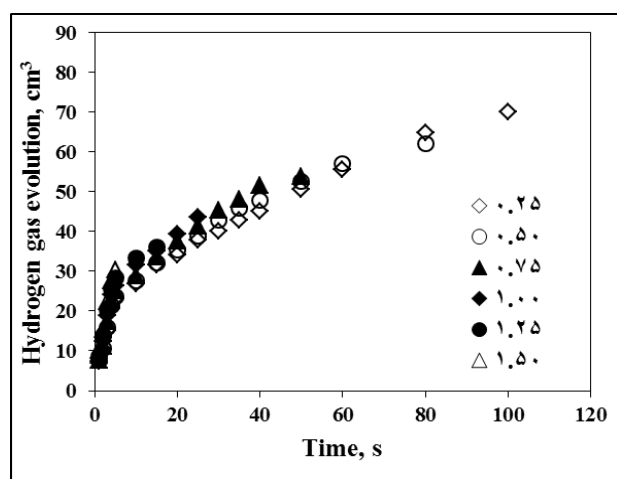

Fig. 2. SEM images of SPC.

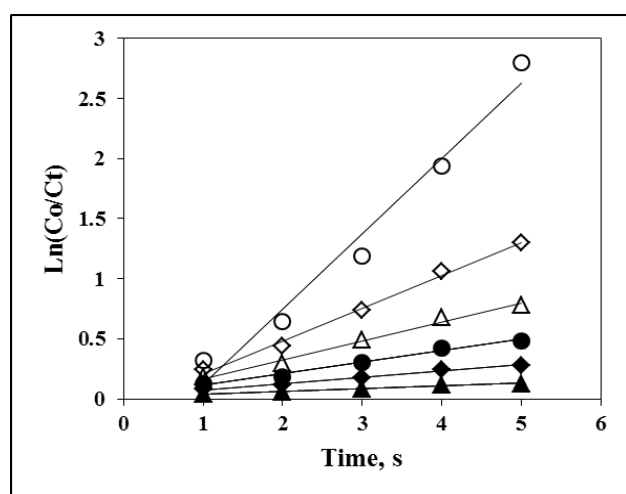**Fig. 3.** The hydrogen generation at various mole ratios of $H^+_{(SPC)}/NaBH_4$.

Fig. 4. The kinetic rate constants of hydrolysis of $NaBH_4$ at various mole ratio of $H^+_{(SPC)}/NaBH_4$.
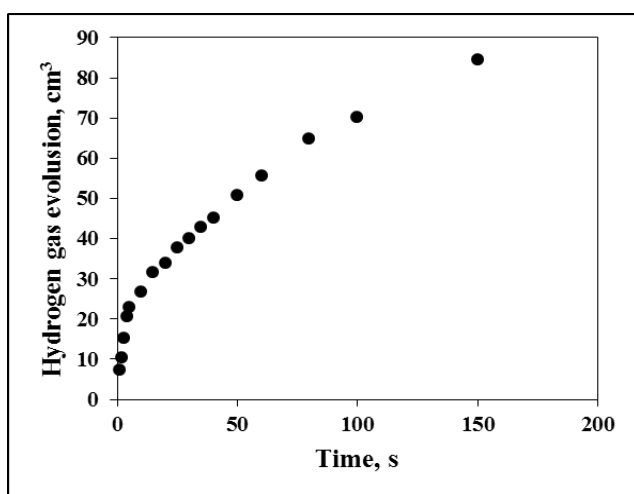

Fig. 5. The hydrogen generation at ratio $H^+_{(SPC)}/NaBH_4$ of 0.25.

The amount of water is excess and therefore, equation (5) is simplified as equation (3). The pseudo-first order kinetic equation was used to calculate the kinetic rate constant of spontaneous hydrolysis of $NaBH_4$ by using the second part of H_2 evolution curve of Fig. 5. The kinetic rate constant of hydrolysis reaction without SPC was 0.003 s^{-1} with R^2=0.987 (Fig. 6). The results are shown an increasing of 7.6 times in kinetic rate constant of $NaBH_4$ hydrolysis reaction at presence of SPC as a solid acid.

3.4. Activation energy

The activation energy was calculated by using the results of hydrogen evolution at ratio $H^+_{(SPC)}/NaBH_4$ of 1 at temperatures of 25, 40, 55 and 70 °C. The Arrenious equation was used to determine the activation energy.

$$k = A\exp(-E_a/RT) \qquad (6)$$

The kinetic rate constants and activation energy are collected in Table 2. The activation energy was 1.24 KJ mol^{-1} for hydrolysis of $NaBH_4$ by using SPC. Apparently, a decrease in activation energy in comparison to liquid-acid such as HCl and CH_3COOH is due to the presence of solid-acid.

3.5. Reusability of the SPC

The reusability of the SPC was tested in 4-cycles in hydrogen generation with $NaBH_4$ at mole ratio 1. After each cycle, the SPC are removed from sample, washed with dilute sulfuric acid and water and dried at 80 °C in 12 h. The reusability of SPC activity in hydrogen generation is shown in Fig. 7. As seen, the treatment of SPC shows the reproducibility of its behavior as an acid/catalyst in hydrogen generation reaction so that a 10% reduction is observed in kinetic rate constant after 4-cycles of experiments.

3.6. Comparison of SPC activity

In order to rationally evaluate the activity of SPC in hydrolysis reaction, a comparative study was made with two solid acids such as Amberlyst-15 and Nafion-NR50 and homogeneous acids of HCl and CH_3COOH. The yield and time of hydrolysis reaction, surface areas of solid acids, acid

Table 1. The pseudo-first-order rate constant (k) and half-life $t_{1/2}$ at different mole ratio of $H^+_{(SPC)}/NaBH_4$ for hydrogen generation.

MR	k_{app}, s^{-1}	$t_{1/2}$, s
0.25	0.023	30.13
0.50	0.052	13.33
0.75	0.095	7.29
1.00	0.157	4.41
1.25	0.272	2.55
1.50	0.626	1.11

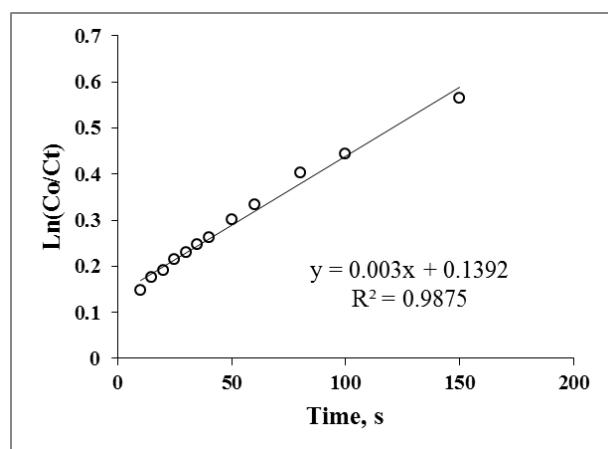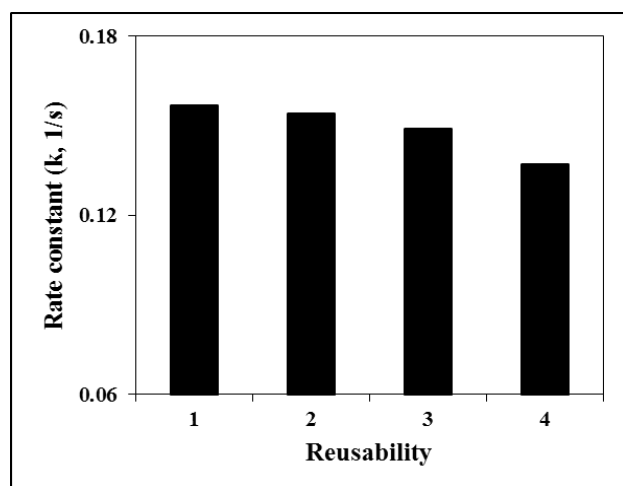**Fig. 6**. The kinetic rate constant of hydrolysis of $NaBH_4$ at ratio $H^+_{(SBC)}/NaBH_4$ of 0.25.

Fig. 7. The repeatability of SPC activity in hydrogen generation.

densities and added amounts of acids are summarized in Table 3. As seen, SPC show a very high surface area and low reaction time in comparison Amberlyst-15 and Nafion-NR50. Also, a reaction time 25 s is obtained at presence of SPC with acid density (mmol H^+/g) of 4.7 that is comparable with HCl and CH_3COOH with high acid density.

Hydrochloric acid, as a homogeneous acid, has the highest activity, reaching 100% yield of H_2 (based on $NaBH_4$) after 40s of reaction [30]. However, among of solid acids with the same chemical equivalent of H^+, the higher activity is observed at presence of SPC. The high activity performance of the SPC is attributable to the high specific surface area and the high density of porous, which provide good access to the SO_3H groups on the surface of the carbon material.

4. Conclusions

A simple producer can be used to prepare Sulfonated Porous Carbon. The prepared SPC can be used as a solid acid in $NaBH_4$ hydrolysis. The kinetic rate constant of hydrolysis

Table 2. The pseudo-first-order rate constant (k) at different temperatures and activation energy of hydrolysis at ratio of $H^+_{(SPC)}/NaBH_4$ of 1.

T, K	k_{app}, s^{-1}
298	0.157
313	0.162
328	0.165
343	0.168
Ea, KJ/mol	1.24
R2	0.988

reaction is 7 times as much in comparison to non-catalyzed hydrolysis. The proposed SPC shows properties such as safety, good proton source, least hazardous, cheapness, availability of the reagents, easy and clean work-up. The hydrolysis reaction is controllable at these conditions. We believe that the present methodology could be novel and important addition to existing methodologies.

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Table 3. Comparison of SPC activity with other acids (mole ratio of $H^+/NaBH_4 =1$).

Acids	Total surface area (m^2/g)	Acid density (mmol H^+/g)	Added amount (g)	Time	Hydrogen generation yield (%)
Nafion-NR50	0.1	0.8	0.625	35 (min)	90
Amberlyst-15	53	4.7	0.106	3 (min)	91
SPC	1260	4.7	0.106	25 (s)	91
CH_3COOH	-	16.6	0.03	100 (s)	90 (21)
HCl	-	27.4	0.018	10 (s)	100 (21)

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