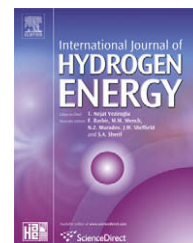


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Improved hydrogen generation from alkaline NaBH_4 solution using cobalt catalysts supported on modified activated carbon

Dongyan Xu^{a,*}, Ping Dai^b, Qingjie Guo^a, Xuehai Yue^a

^aCollege of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China

^bCollege of Electromechanical Engineering, Qingdao University of Science and Technology, Qingdao 266061, PR China

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ABSTRACT

Hydrogen production from alkaline sodium borohydride (NaBH_4) solution via hydrolysis process over activated carbon supported cobalt catalysts is studied. Activated carbons are used in their original form and after liquid phase oxidation with HNO_3 . The changes in surface functional groups of the activated carbon are detected by FTIR spectroscopy. The effects of HNO_3 oxidation on the properties of the activated carbon and the resulting catalyst performance are investigated. FTIR analysis reveals that the oxidative treatment leads to the formation of various functional groups on the surface of the activated carbon. Cobalt catalysts supported on the modified activated carbon are found to exhibit higher activity and stability.

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1. Introduction

With growing concerns over energy and environment problems, proton exchange membrane fuel cells (PEMFCs) are attracting more and more attentions as clean and efficient power generation devices. However, their commercialization is still lagging behind, mainly due to their high cost and a lack of hydrogen infrastructure.

Hydrogen can be stored in tanks as compressed or liquefied H_2 , in hydrogen storage alloys, and on activated carbon or nanoscale materials such as carbon nanotubes. Unfortunately, their volumetric and gravimetric efficiencies are still too low to meet the requirements, whereas liquid fuels (methanol, ethanol, gasoline, etc.) and chemical hydrides (NaBH_4 , KBH_4 , LiH , NaH , etc.) are becoming increasingly important as

a potential route to supply hydrogen for the PEMFCs. However, in the case of the liquid fuels, high-temperature reforming processes are too complex to satisfy the requirements of portable PEMFCs operation. Instead, hydrolysis of sodium borohydride has been intensively investigated as an ideal source of hydrogen for PEMFCs due to its high-energy density and easy control of hydrogen generation rate on demand [1–3].

To inhibit the self-hydrolysis reaction, NaBH_4 solutions are usually maintained as a strong alkaline solution by adding NaOH , meaning that the hydrogen generation performance from hydrolysis of alkaline NaBH_4 is dependent on the usage of catalysts to a great extent. Up to now, the most studies on hydrolysis catalysts are mainly centered on nickel borides [4], cobalt borides [5], precious metals supported on anionic exchange resin [6] and LiCoO_2 [7].

* Corresponding author. Tel.: +86 532 84022506; fax: +86 532 84022757.

E-mail address: xdy0156@sina.com.cn (D. Xu).

The hydrolysis of NaBH_4 is highly exothermic with heat of reaction of ca. 210 kJ/mol, implying that the catalyst in the hydrolysis of NaBH_4 is exposed to a hot caustic environment, especially when the reactor is operated in a continuous flow mode [8]. Activated carbons exhibit high specific surface area and high chemical stability in aggressive environments (e.g. concentrated solutions of acids or bases). Therefore, activated carbon is particularly appropriate to be used as supports for metal catalysts manufacture to provide optimum properties and stability for hydrolysis of alkaline NaBH_4 . It has been reported by many researchers [9–11] that the surface oxygen-containing functional groups, which form anchoring sites for metallic precursors as well as for metals, dominantly determine the properties of activated carbon as a catalyst support material, especially for precious metal catalysts. Surface oxygen complexes are formed on activated carbons when they are treated with oxidizing agents by different dry and wet methods [12]. In general, the order of the extent of oxidation produced is $\text{HNO}_3 > \text{H}_2\text{O}_2 > \text{air}$, and it is almost independent of the porosity of the treated carbon [13].

In this study, a commercial activated carbon was used as supports, as received or after oxidation by HNO_3 . The effects of oxidation on the textural and chemical structure of activated carbon were investigated. Activated carbon supported cobalt catalysts were prepared by impregnation-chemical reduction method. The as-prepared catalysts were used for the hydrolysis of alkaline NaBH_4 , and the catalyst performance was evaluated.

2. Experimental

2.1. Oxidation of carbon samples

A commercial activated carbon (denoted as AC) was ground and sieved to 20–30 mesh prior to its use. The AC was chemically modified with aqueous solutions of HNO_3 in order to increase the concentration of surface oxygen-containing groups, and thus determine the effect of surface modification of the AC on catalyst properties. The chemical modification was performed by adding 5 g AC into 50 mL 30% HNO_3 solution, and maintaining at 60 °C for 7 h. After completion of the oxidation process the AC sample was carefully washed with distilled water and dried at 383 K overnight. The samples untreated and via modification with 30% HNO_3 solution are denoted as AC0 and AC1, respectively.

2.2. Catalyst preparation

The catalysts were prepared by impregnation-chemical reduction method. In a typical preparation procedure, a certain amount of commercial AC0 or AC1 was impregnated with an aqueous solution of cobalt nitrate. After drying at 100 °C for 12 h, a certain amount of fresh-prepared 5 wt% NaBH_4 solution was dropped slowly into the catalyst precursor. Then, the sample was filtered, washed with distilled water several times, and dried at 100 °C for 10 h. At last, the catalyst was calcined under nitrogen atmosphere at 300 °C. The cobalt loading in the as-prepared catalysts is 10 wt%. The as-prepared catalysts with untreated and modified AC supports are denoted as Co/AC0 and Co/AC1, respectively.

2.3. Characterization

The textural properties of the untreated and modified AC samples were determined by nitrogen adsorption at 77 K with an ASAP 2010 surface area analyzer (Micromeritics Instrument). Before measurements, the samples were dried at 383 K for 12 h and out-gassed at 523 K under vacuum. Surface area was calculated following the BET method.

The surface functional groups on the untreated and modified AC samples were examined using Fourier transform infrared spectrometer (FTIR-380). The spectra were recorded from 4000 to 500 cm^{-1} .

Powder X-ray diffraction patterns of the as-synthesized catalysts were obtained with a D8 ADVANCE X-ray diffractometer using Cu K_α radiation operating at 40 kV and 50 mA. The angle extended from 10 to 80° and varied with a step of 0.05°.

2.4. Catalyst testing

For the convenience of preparing the reactant solutions, all the solution concentrations used in our study were expressed as the ratio of weight of NaBH_4 or NaOH to solution volume.

In a typical batch hydrogen generation experiment, 10 ml 5% NaBH_4 –1% NaOH solution was initially put into the flask. The hydrolysis reaction was initiated by dropping an amounted catalyst (0.25 g) into the solution quickly. The flask was immersed in a water bath to maintain the temperature at relatively constant value. During the reaction, a wet gas meter was used to measure the cumulative volume of the generated hydrogen over time. Because the evolved hydrogen can generate vigorous bubble in the reactor and facilitate the contact between the reactant and the catalysts, no further stirring was adopted during the reaction.

For a successive hydrogen generation experiment, a stainless-steel tubular reactor was adopted. A certain amount of catalyst was placed in the reactor prior to the reaction. The system was sealed, and then 10% NaBH_4 –5% NaOH solution was pumped from a storage tank into the reactor with a certain flow rate. The generated hydrogen, the by-product and the residual reactant solution were imported into a gas-liquid separator. The system was not preheated, and no attempt was made to control the temperature of the experimental system during testing.

3. Results and discussion

3.1. Textural characterization

The nitrogen adsorption isotherms of the untreated and modified AC samples are shown in Fig. 1. It is apparent that the adsorption isotherms of AC exhibited a steep initial uptake, indicating microporous character of the carbons. In addition, the oxidation of AC leads to the downward shift of the isotherm. Similar change of isotherms has been observed by previous workers for different activated carbon samples [12,14]. The textural properties of the untreated and modified AC samples are presented in Table 1. After oxidation, the specific surface area and the total pore volume of AC

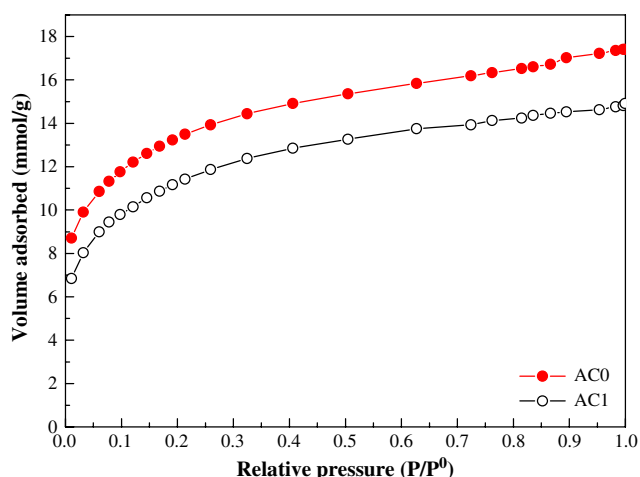


Fig. 1 – Nitrogen adsorption isotherms of untreated and modified AC samples at 77 K.

decreased from 1035 m²/g and 0.61 cm³/g to 895 m²/g and 0.49 cm³/g, respectively. Some researchers have attributed this observation to pore entrance blockage by the formation of oxygen functional complexes introduced by nitric acid treatment [14].

3.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was employed to explore changes in functional groups induced by modification. FTIR spectra for the untreated and HNO₃ oxidised AC samples are depicted in Fig. 2. The results show some pronounced bands at 1040, 1630, and 3450 cm⁻¹. The spectra for AC0 and AC1 show some marked similarities, suggesting that they could possess similar groups on their surfaces, and that no significant chemical changes occurred during HNO₃ oxidation. However, nitric acid oxidation modifies the intensities of existing bands in original AC.

Between 800 and 1300 cm⁻¹ a broad band is observed, which is a superposition of a number of broad overlapping bands of ether, epoxide and phenolic structures in different environments [15,16]. A strong absorption band was observed at around 3450 cm⁻¹ and this is assigned to O–H stretching vibrations of surface hydroxylic groups and chemisorbed water [17,18]. It is obvious that the relative intensity of this band increased markedly after HNO₃ oxidation, suggesting that the oxidation of AC by HNO₃ generates a large number of carboxyl groups. The band at 1630 cm⁻¹ can be attributed to O–H deformation vibration of carboxyl group and/or to the

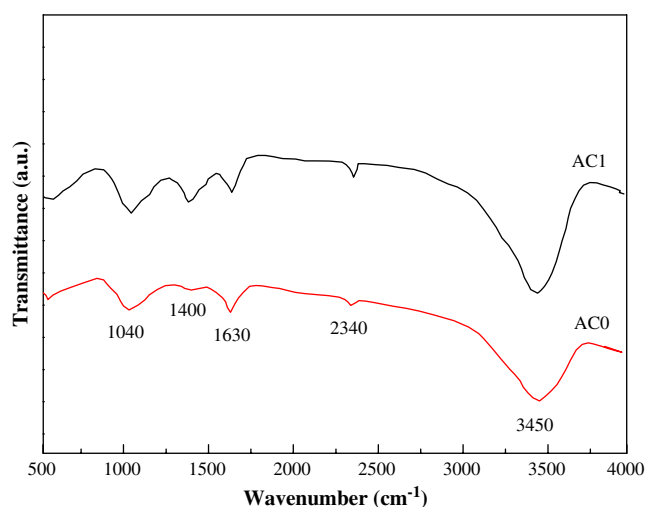


Fig. 2 – FTIR spectra of untreated and modified AC samples.

existence of carboxyl-carbonate structures [12,19]. This band is also a characteristic peak for carbon materials and is probably ascribable to carbonyl groups which are highly conjugated in the graphene layer such as quinone and/or ionoradical structure C=O [20]. For AC0 sample, the weak band appearing at about 1400 cm⁻¹ is ascribed to the symmetrical COO⁻ vibrations [20]. For the oxidized samples (AC1), the relative intensity of this band increases. A very weak band centered near 2340 cm⁻¹ can be seen in FTIR of AC0 and AC1 samples. Such bands have also been observed in earlier IR studies of carbon [12] and are assigned to carbon-oxygen groups due to a ketone.

3.3. X-ray diffraction measurements (XRD)

XRD profiles of cobalt catalysts supported on the untreated and modified AC are shown in Fig. 3. It is expected that amorphous Co-B could be formed on the surface of AC support after cobalt precursor reduction with NaBH₄. The

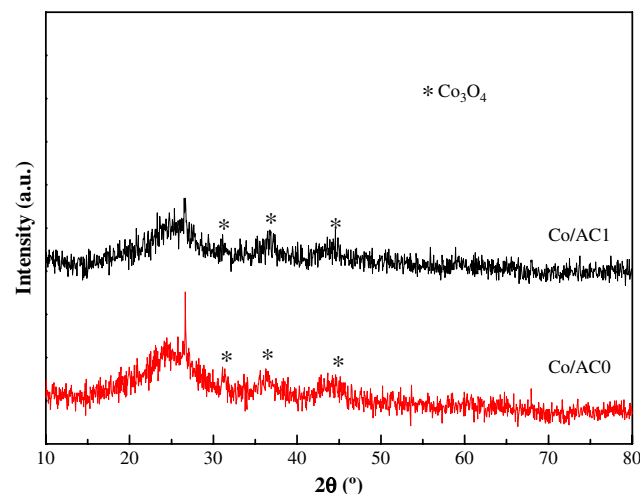


Fig. 3 – XRD patterns of cobalt catalysts supported on untreated and modified AC.

Table 1 – Textural properties of untreated and modified activated carbon samples.^a

Sample	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)
AC0	1035	0.61	0.46
AC1	895	0.49	0.39

^a S_{BET} = BET surface area; V_{total} = total pore volume; V_{micro} = micropore volume by t-method.

fresh calcined catalyst, however, displays several peaks at 31.1, 36.6, and 44.3°, which are ascribed to different crystal planes of Co_3O_4 . It was reported the formation of Co_3O_4 when Co–B powder was passivated in the N_2 atmosphere mixed with 1% air [21]. Therefore, weak oxidation of amorphous Co–B on the surface of AC may have occurred during calcination under N_2 atmosphere containing trace oxygen.

3.4. Catalytic hydrolysis of NaBH_4

Fig. 4 presents the hydrolysis activities of cobalt catalysts supported on original and modified AC. The rates of hydrogen generation were measured from 10 ml 5% NaBH_4 solution containing 1% NaOH in a batch operation. As presented in Fig. 4, the cobalt catalysts supported on modified AC exhibited higher activity than that supported on original AC, suggesting that the modification of AC with HNO_3 leads to the improvement of catalyst performance, possibly due to the increase of functional groups on the surface of AC which is beneficial to the dispersion of cobalt metals. In fact, the oxidative treatment influences both textural properties and chemical properties of the AC. Therefore, the effects of oxidative treatment of AC support on final catalytic properties is rather complicated, and further studies are necessary to explore the nature of the effects of AC oxidation on supported catalyst properties and to optimize further the catalyst performance.

Hydrolysis kinetics is not only dependent on catalyst performance, but also on other factors, such as NaBH_4 concentration, NaOH concentration, and reaction temperature. It is obvious that a higher NaBH_4 concentration would provide more hydrogen density, which is particularly attractive in PEMFCs applications. In order to understand the effects of initial NaBH_4 concentrations on the hydrogen generation rate, a set of experiments were performed with the NaBH_4 concentrations varied from 5 to 25% while the NaOH concentration was held constant at 1% using 0.25 g of Co/AC1 catalyst. Fig. 5 shows the effects of initial NaBH_4 concentrations on the reaction at 30 °C. As NaBH_4 concentration increased from 5 to 15%, the hydrogen generation rate

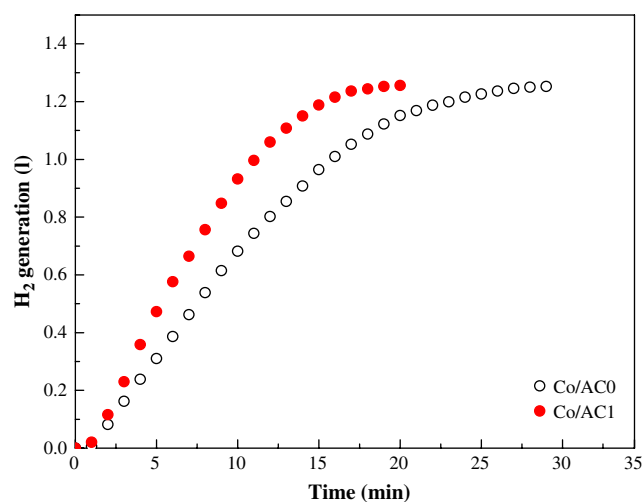


Fig. 4 – Behavior of hydrogen generation over cobalt catalysts supported on untreated and modified AC.

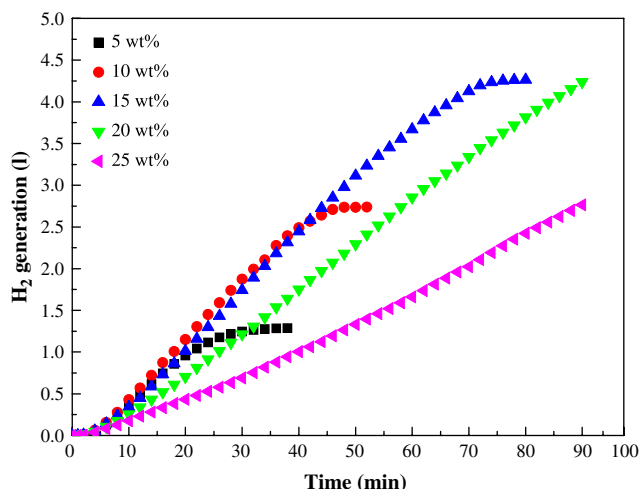


Fig. 5 – Effect of sodium borohydride concentration on hydrogen generation.

changes little. However, the rate decreases markedly when NaBH_4 concentration increased from 15 to 25%. A similar observation has been made by Krishnan et al. on resin supported catalyst [7]. They suggested that the decrease of hydrogen generation rate at high NaBH_4 concentration above 10 wt% may be due to an increase in the pH value of the concentrated solutions with a resulting increase in their stability. It must be noted that many researchers [6,22] had found that the hydrogen generation rate decreases with NaBH_4 concentration both at low and high concentrations, which is reasonable to be ascribed to the increase of solution viscosity. The increase of the solution viscosity may cause mass-transport limitations of borohydride from the solution to the surface of catalyst. Recently, Moon et al. [23] reported that the experiments were carried out without alkali-stabilizer in order to clarify the inherent hydrogen storage capacities according to changes in NaBH_4 concentration (5–25 wt%). It is found that when the NaBH_4 concentration increased from 15 to 20 wt%, the difference in hydrogen generation rate was minimal. For 25 wt% NaBH_4 , the rate of hydrogen generation actually decreased. The authors ascribed these results to the reduced water activity at higher NaBH_4 concentration.

Generally, the chemical reaction rate increases with the reactor or solution temperature. Kinetic studies at varied temperatures were further carried out using the optimized catalyst. Fig. 6 presents the hydrogen generation kinetic curves at a solution temperature ranging from 20 to 40 °C. To minimize the effect of temperature changes resulted by the exothermic hydrolysis reaction, this set of experiments was carried out using 1% NaBH_4 –1% NaOH solution. This measure allows the solution temperature to be controlled to within ± 1 °C during the reaction. As expected, the initial hydrogen generation rate increases significantly with an increase in temperature. The influence of temperature is clearly shown by both the increasing slope values on the linear region of the plots and the decreasing induction period (as shown in the inset of Fig. 6).

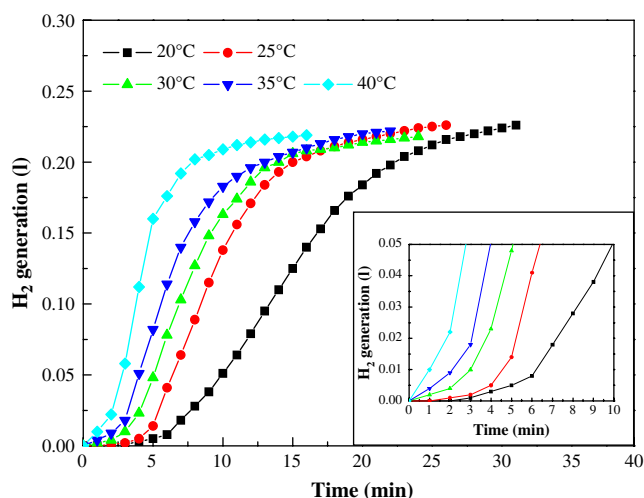


Fig. 6 – Kinetic curves for hydrogen generation by hydrolysis of 1% $NaBH_4$ + 1% NaOH solution at varied temperatures.

To control the hydrogen generation rate, basic-stabilizer, such as NaOH, was added to $NaBH_4$ solution to make the solution basic. Fig. 7 demonstrates hydrogen generation rate measured from 5% $NaBH_4$ -x% NaOH (x = 1, 5, 10, 15) solution at 30 °C using 0.25 g of catalyst. With increasing NaOH concentration from 1 to 5%, the steady-state hydrogen generation rate increases. However, the hydrogen generation rate decreases significantly when NaOH concentration increased from 5 to 15%. Although many researchers have investigated the effects of NaOH concentration on hydrogen generation behaviors, very different even opposite results were arrived. As demonstrated by Amendola et al. [6], the solubility of sodium metaborate reaction product decreased with an increase in NaOH concentration. This reduced hydrogen generation rates as weight percent NaOH increases from 1 to 5 wt%, and then to 10 wt% using Ru supported on IRA-400 anion exchange resin catalyst. Also with Ru/IR-120 catalyst, Hsueh et al. [24] reported that the initial H_2 generation rate decreases from 120 to a minimum of $31 \text{ ml min}^{-1} \text{ g}^{-1}$ catalyst with the NaOH concentration increases from 1 to 15%.

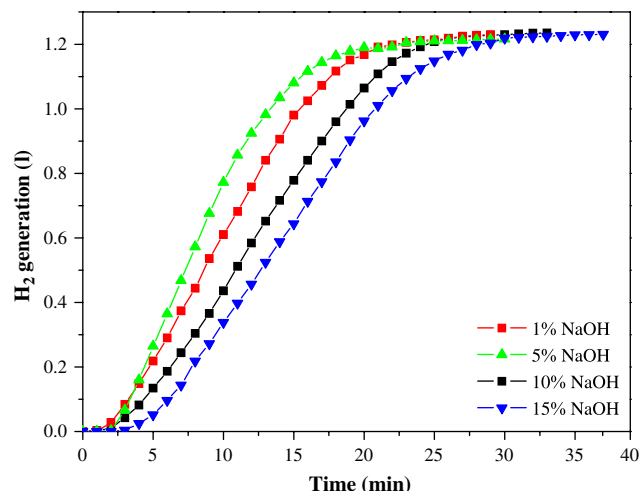


Fig. 7 – Effect of sodium hydroxide concentration on hydrogen generation.

Other authors also reported similar results obtained using Co-B [22] and Pt(Ru)/LiCoO₂ [25] catalysts. Whereas Dong et al. [4] reported a completely different results about the effects of NaOH concentration on the $NaBH_4$ hydrolysis rate in the case of Ni_xB catalyzed reaction. It was found that the hydrogen generation proceeded very moderately in the absence of NaOH and became accelerated with increasing NaOH concentration, demonstrating an enhancement of reaction by NaOH. Pinto et al. [26] also reported the enhanced effect of NaOH on hydrogen generation both at low and high $NaBH_4$ concentrations with nickel-based power catalyst. In the case of Ni power catalyst [27], it was found that the addition of NaOH exhibited no influence on hydrogen generation rate when NaOH concentration was less than 20 wt%. However, when NaOH concentration was increased to 30 wt%, hydrogen generation rate decreased. A similar results obtained using Ni-Co-B catalyst was reported by Ingersoll et al. [28]. These different results indicate that the influence of NaOH on the hydrogen generation rate depends largely on the catalysts used in the investigations.

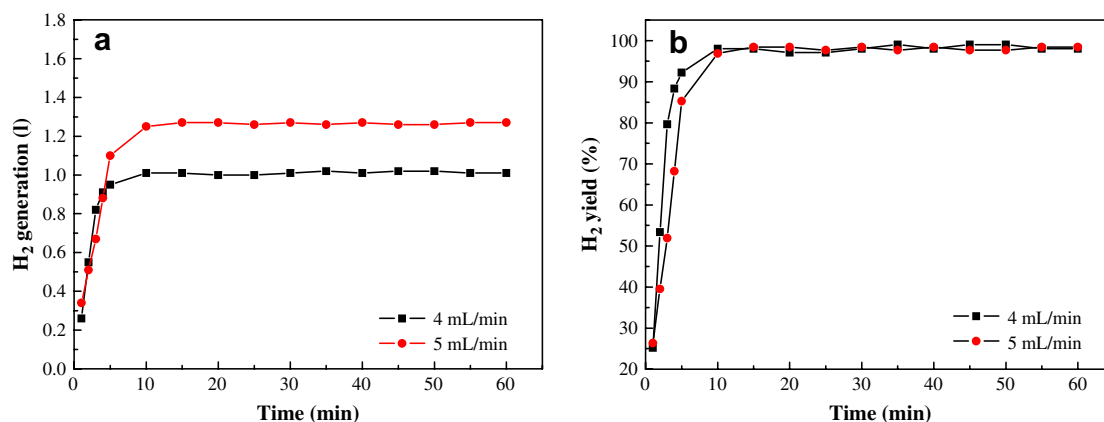


Fig. 8 – Behavior of hydrogen generation in successive reaction at different feed flow rates (a) hydrogen generation rate; (b) hydrogen yield.

To detect the stability of Co/AC catalyst, the behavior of hydrogen generation in successive reaction was also investigated. Fig. 8 shows the successive hydrogen generation performance of Co/AC catalyst at the feed flow rate of 4 mL min^{-1} and 5 mL min^{-1} . The hydrogen generation rate increased gradually in the first few minutes and then reached a steady value (Fig. 8(a)). No decrease in hydrogen generation rate was observed during the testing period, suggesting the good stability of Co/AC catalyst. The steady state was also reflected by the relatively constant reaction temperature maintained at about 370 K. In addition, high hydrogen yields were also obtained under the reaction conditions (Fig. 8(b)).

4. Conclusion

It was established that oxidative treatments of activated carbon with 30% HNO_3 exhibited influence on both textural properties and chemical properties of AC. The oxidation of AC by HNO_3 generates a large number of functional groups but at a cost of specific surface area and pore volume decreases to some extent. The oxidative treatments of activated carbon lead to the improvement of supported cobalt catalyst's performance, possibly due to the increase of functional groups on the surface of the AC which is beneficial to the dispersion of cobalt metals. Temperature increases contribute significantly to the hydrogen generation rate. Increases in NaBH_4 concentrations higher than 10% result in negative effect on hydrogen generation rate. The Co/AC catalysts exhibit quick response and good durability in the successive reaction.

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