Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Letters 60 (2006) 2236–2239
materials letters
www.elsevier.com/locate/matlet

Carbon-supported platinum catalysts for on-site hydrogen generation from $NaBH_4$ solution

Ying Bai [a,b], Chuan Wu [a,b,c,*], Feng Wu [a,b], Baolian Yi [c]

[a] School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China
[b] National Development Center for High Technology Green Materials, Beijing 100081, China
[c] Fuel Cell R&D Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Received 1 July 2005; accepted 29 December 2005
Available online 19 January 2006

Abstract

A flexible hydrogen generation (HG) method based on catalytic hydrolysis of $NaBH_4$ solution is developed. Carbon-supported platinum (Pt/C) samples served as the catalysts, and the catalytic strategies for hydrolysis of $NaBH_4$ solution are analyzed via the studies on apparent morphology, catalytic activity, BET surface, and sustaining H_2 supply test. Pt/C catalysts are proved to be excellent accelerators, and Pt-loading plays an important role in the hydrogen generation reactions. For a reactor loaded with 100 mg 13.1% Pt/C catalyst, when 10% $NaBH_4$–5% NaOH solution is pumped into the reactor with a speed of 10 ml/min, it can achieve a maximum HG rate of 29.6 (l/min/g catalyst), and give sustaining H_2 supply for a proton exchange membrane fuel cell (PEMFC) with an average HG rate of 23.0 (l/min/g catalyst).

Keywords: Hydrogen generation; $NaBH_4$; Catalytic hydrolysis; Pt/C catalyst; Proton exchange membrane fuel cell

1. Introduction

Since the mid-19th century, global energy systems have experienced transitions from wood and hay to coal and nuclear, then to oil and hydrocarbons, then to natural gas and hydrogen. Namely, global energy sources have a tendency of shifting from solids to liquids, and from liquids to gases. According to the prediction of energy toward sustainable economic growth [1], it is coming the age of energy gases, especially the age of hydrogen.

Pure hydrogen is adopted as the fuel in PEMFC. The currently used hydrogen is mostly produced from natural gas via catalytic reforming, or from electrolysis of water. However, for a mobile PEMFC, these H_2 supply methods are not quick and flexible enough. Therefore, small-scaled hydrogen generation (HG) method, which can quickly provide pure H_2, is the most important issue in supplying the mobile PEMFC.

So far, many efforts are focusing on chemical techniques for hydrogen generation [2–5]. At 25 °C, the concentration of saturated sodium borohydride ($NaBH_4$) solution is 35 wt.%, and has a maximum H_2 storage mass of 7.4% according to Eq. (1), which is higher than many other metal hydrides and hydrocarbons [6]. Only when selected catalysts are added, it can release hydrogen rapidly in the following way:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2,\ \Delta H = -217\text{kJ/mol}. \quad (1)$$

According to the study of Brown and Brown [7], aqueous solutions of platinum, ruthenium and rhodium salts can be reduced by aqueous $NaBH_4$ solution. More recent studies show that some precious metal-based catalysts, such as IRA-400 supported ruthenium [8,9] or metal oxide supported platinum

* Corresponding author. School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China. Tel.: +86 10 68912508; fax: +86 10 68451429.
E-mail address: chuanwu@bit.edu.cn (C. Wu).

0167-577X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.12.119

Table 1
Pt-loadings of Pt/C catalysts obtained by EDXA

Sample	A	B	C
Pt-loading (%)	1.84	6.88	13.1

[10], have good catalytic activities. In this paper, Pt/C catalysts serve as the catalysts, and the catalytic strategies for hydrolysis of $NaBH_4$ solution are analyzed via the studies on apparent morphology, catalytic activity, BET surface, and sustaining on-site H_2 supply test.

2. Experimental

2.1. Sample preparation

A carbon support with a 235 m^2/g BET surface area, Vulcan XC-72R, was selected as catalytic supports. An impregnation method [11] was adopted to obtain Pt/C catalysts with different Pt-loadings; the carbon support was first impregnated in 0.04 mol/l chloroplatinic acid solution with the volume correspondent with the designed Pt-loading for 24 h, and then calcined in a reductive gas atmosphere at 300 °C for 2 h.

2.2. SEM investigation

The morphologies of the as-prepared Pt/C catalysts were observed on a JSM-35C scanning electron microscope (SEM), and the Pt-loading of the catalysts were obtained by energy dispersive X-ray analysis (EDXA).

2.3. BET analysis

Nitrogen adsorption of the samples was measured at −196 °C with an ASAP 2010 surface area analyzer (Micromeritics Instrument). Prior to the measurements, the sample was vacuum-dried at 110 °C for 12 h to remove residual water and gases. The specific surface of the sample was determined from the N_2 adsorption–desorption isotherms by BET method.

2.4. Catalytic activity test

To test the HG performances of the as-prepared Pt-based catalysts, two reaction modes were adopted. For an intermittent reaction, Pt-based catalyst was placed in a HG reactor in advance, and then 10 ml 5% $NaBH_4$–10% NaOH solution was dropped into the reactor quickly. During the catalytic hydrolysis reaction of $NaBH_4$, a flowmeter was adopted to record the cumulative volume of the generated H_2. After the hydrolysis reaction stopped, the residual liquid was removed from the reactor, while the catalyst particles were reserved.

For a successive reaction, 100 mg catalyst was placed in a reactor prior to the HG reaction. Then, the system was sealed, and pure nitrogen gas was fed in to drive the air away from the system. After that, 10% $NaBH_4$–5% NaOH solution was pumped from a storage tank to the reactor with a speed of 10 ml/min; and the catalysis hydrolysis reaction processed on the catalyst bed successively. 20 min later, the pump was stopped. The generated H_2 was imported into a special bottle to wash out the residual alkali and water, and then cooled to ambient temperature. Subsequently, the as-processed H_2 was imported

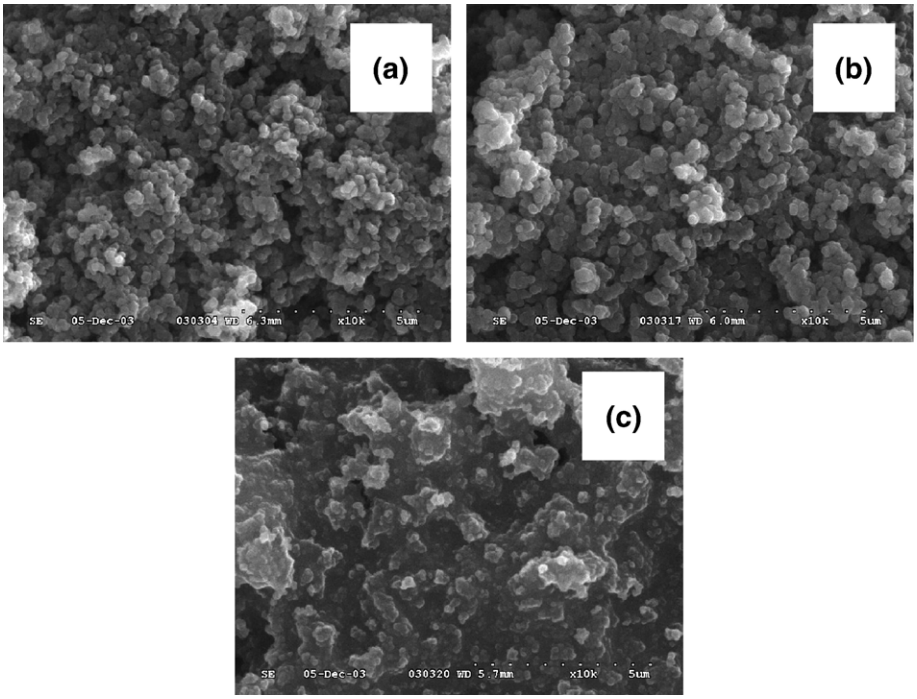

Fig. 1. SEM images of Pt/C catalysts with Pt-loadings of (a) 1.84%, (b) 6.88%, and (c) 13.1%, respectively.