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ScienceDirect
Catalysis Today 120 (2007) 63–70
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Pd-Zn/Cu-Zn-Al catalysts prepared for methanol oxidation reforming in microchannel reactors

Guangwen Chen *, Shulian Li, Quan Yuan

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Available online 14 August 2006

Abstract

Methanol oxidation reforming is an important reaction in the process of hydrogen generation for PEMFC. In this paper, we report the wall coated catalysts in a microchannel reactor for methanol oxidation reforming. The preparation method of the wall coating catalyst was studied in detail, i.e., the sol–gel and solution-coating techniques. To prepare the catalysts for methanol oxidation reforming, the washing-coating layer of CuZnAl was prepared by the sol–gel technique, and then the active layer was coated on it by solution-coating technique with emulsion colloid containing Pd–ZnO particles. Both the supporting layer and catalyst on the stainless steel foils were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The formed wash-coating layer with ordered arrays of petaloid microcrystallites in layer surface and Pd–Zn alloy crystal phase can be clearly observed. The reaction experimental results indicated that the catalyst prepared have high activity and relatively high stability.

Keywords: Microchannel; Microstructured reactor; Wall coating; Oxidation reforming; Microreactor

1. Introduction

Automotive exhaust is currently one of the major pollution sources. As a pollution-free and energy-saving power supply for electric vehicles, the fuel cell is the best candidate with its high energy conversion efficiency (50–70%) and zero or nearly zero emission. Hydrogen is the fuel for proton exchange membrane fuel cell (PEMFC). The on-board generation of hydrogen from methanol was known as the one of most practical ways for proton exchange membrane (PEM) fuel cells vehicle [1]. However, the miniaturization of hydrogen source is the prerequisite for its practical application [2,3].

Technology for converting methanol into a hydrogen-rich supply for the fuel cells is mainly based on steam reforming, partial oxidation or a combination of both, namely oxidation steam reforming or oxidation reforming or autothermal reforming, in which the methanol oxidation reforming is the most promising way due to its energy saving, fast start-up and quick response of the whole system. Due to thermodynamic constrains of methanol reforming, significant amount of CO as a poisoning impurity of platinum electro-catalyst is produced. It is also necessary to reduce the level of CO in the hydrogen-rich gas to less than 50 ppm, although high CO-resistant electro-catalysts were developed, so the process of preferential oxidation of CO is required.

Great achievements have been reported in the new area of microreactor technology [4,5], it is now attainable to use microchannel reactors in the field of on-board PEMFC hydrogen source via methanol conversion [6]. The small dimension of microchannel geometry is favoring isothermal operating conditions due to high surface-to-volume ratio, enhanced heat and mass transfer and intrinsic safety. The application of microreaction technology can greatly improve the efficiency of systems and diminish their volumes and weights. The review article [6] has made a deep discussion on the developments in portable hydrogen production using microreactor technology. However, catalyst immobilization into the microchannels is still a challenge which is influenced by a low interaction between metallic plate surfaces and catalyst carriers. [7–9].

Three main ways were applied for catalyst immobilization in microchannel, the one is that the reactors or microchannels themselves were made of active materials [10–13], the two others are wall-coating technique and catalysts packed into channels in the form of powder, small pellets or structured strips

* Corresponding author. Tel.: +86 411 84379031; fax: +86 411 4691570.
E-mail address: gwchen@dicp.ac.cn (G. Chen).

0920-5861/$ – see front matter
doi:10.1016/j.cattod.2006.07.004

[14,15], respectively. The shortcoming of the former is much evident due to its low surface-to-volume ratio and low utilization of noble metal, so it is limited in laboratory, while the pressure drop in the microchannels packed with catalysts is somewhat higher due to their small size. In most practical processes, the surface of microchannels must be modified, i.e., with wash-coating layer as catalyst support. The methods can not only enhance the surface-to-volume, but also improve the utilization of active components. The main wall-coating techniques developed are, e.g., preparation of alumina by a CVD process [16], sol–gel methods [17], anodic oxidation of aluminum inside microchannels [18,19], impregnation [20] or solution coating or dip-coating [21], in situ branching polymerization [8], sputtering [22] and hydrothermal synthesis of zeolites [23,24].

The goal of our study was to immobilize the catalyst of Pd-Zn/Cu-Zn-Al for methanol oxidation reforming on the wall of the stainless steel channels. In this paper, we report the methods to immobilize the catalyst in microchannel and to show potential miniaturization of microreactor used in the hydrogen generation system via methanol oxidative reforming. The catalysts were prepared by sol–gel method for wash-coating layer with Cu-Zn-Al and solution-coating method for active layer with emulsion colloid of Pd–Zn particles.

2. Experimental

2.1. Microreactor design

Fig. 1 shows a stainless steel chip of the microreactor made by a chemical etching method. Forty-eight microchannels per chip were separated by 500 μm fins; its width, depth and length were 500 μm, 170 μm and 30 mm, respectively. The entrance and exit areas are triangular shaped with inlets and outlets on opposite sides of the channels array. Volume of microreactor made of four chips was 0.75 ml including microchannels, entrance and exit sections. Prior to prepare catalyst, the metal substrates were cleaned by Na_2SiO_3 solution with the concentration of 30–50 g/l used as emulsifier to remove any oily substances at the temperature of 75 °C and under agitation, then were rinsed with distilled water at the temperature of 60 °C, and cleaned by acetone and de-ionized water, successively. Finally, metal substrates were dried at 110 °C for 2 h [25].

The stainless steel chips with dry and calcined catalyst deposited in the microchannel were assembled into micro-reactor with high heat-resistant inorganic glue and screw-fastening with bolts to assure hermeticity. The exterior structure of microchannel reactor was shown in Fig. 2 [26]. The microreactor consists of four stacked plates and a plate in the middle of them, which is used to control and measure the reaction temperature. The reactant mixture enters through an inlet tube, then flows through the parallel channels and collected in an outlet device. The inlets and outlets of the microreactor are placed on opposite sides of the stack of plates.

2.2. Experimental set-up

The methanol oxidation reforming was carried out in a microchannel reactor at atmospheric pressure. The micro-channel reactor used in this work and the schematic diagram of the testing system were shown in Fig. 3. Prior to the reaction, the catalyst was reduced in situ in a stream of 10% H_2 in N_2 (50 ml/min) at 400 °C for 2 h. The molar ratio of H_2O and O_2 to MeOH in the feed was 1.2 and 0.3, respectively. The mixture of methanol and water was pumped into a vaporizer kept at 200 °C by a micro liquid pump and conveyed into the reactor by air used for carrier gas and oxidant, while N_2 in air as internal standard for product analysis. The air flow was adjusted precisely by a mass flow controller. The reaction temperature in microreactor was controlled at the range of 450–600 °C, gas hourly space velocity (GHSV) was kept at 20,000–180,000 h^{-1}.

2.3. Gas analysis and calculation

The effluent of the reactor was consisted of H_2, CO_2, CO, CH_4 and N_2 as well as H_2O and/or methanol, while CH_4 in effluent is negligible during the experiments. After reaction, the product gases were passed through a cold trap (mixture of ice and water) and a dryer to remove water and methanol, while the dry gas entered an on-line gas chromatograph (GC, 4000A, Beijing East & West Analytical Instruments Inc.) equipped

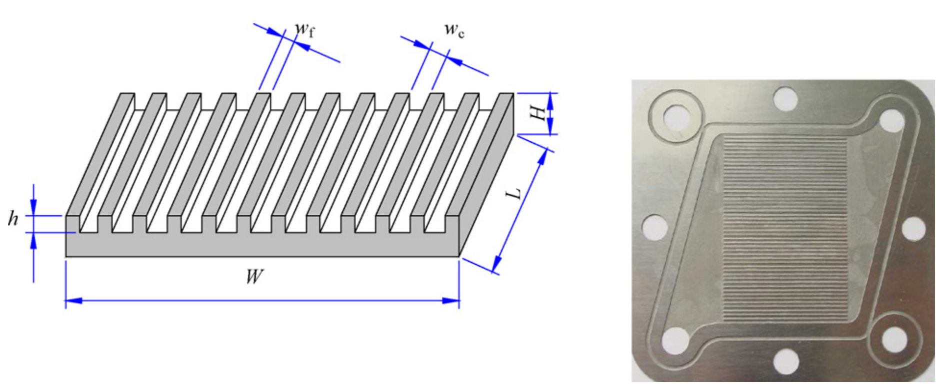

Fig. 1. Chip of microchannel reactor. *W*, width of total channels; w_c, width of single channel; w_f, width of fin; *h*, depth of channel; *H*, thickness of chip; *L*, length of channel.