

Method of catalyst coating in micro-reactors for methanol steam reforming

Sun-Mi Hwang, Oh Joong Kwon, Jae Jeong Kim*

Research Center for Energy Conversion and Storage, School of Chemical and Biological Engineering, Seoul National University, San 56-1, Shillim-dong, Kwanak-gu, Seoul 151-742, Republic of Korea

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Abstract

Micro-channels of silicon-based micro-reactors were successfully coated with deionized (DI) water-based Cu–ZnO–Al₂O₃ catalyst slurry by a fill-and-dry coating method, applicable to pre-assembled micro-reactors, for steam reforming of methanol. The 10–20 μm thick catalyst layers could be formed on the inner walls of the micro-channels after the micro-channels were fully filled with catalyst slurry, because the catalyst particles in the slurry cohered to the walls of micro-channels by surface tension during drying and calcinations. The adhesion between the catalyst layer and silicon surface was improved by pre-coating the micro-channels with an alumina adhesion layer. The addition of polyvinyl alcohol (PVA) in the alumina sol resulted in better adhesion of the alumina layer at the corners of the channels. The critical minimum thickness of the alumina layer for catalyst coating was 0.15 μm. The highest catalytic activity without loss of intrinsic catalytic activity was obtained using 1:5 (catalyst to solvent) DI water-based catalyst layers coated by fill-and-dry coating. The maximum H₂ production rate was 85 ccm with 1650 ppm of CO measured at 300 °C using a methanol feed rate of 9 ml/h.

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1. Introduction

Recently, much attention has been paid to proton exchange membrane fuel cells (PEMFC) as a clean and efficient source of electrical power for portable and microdevices. There are several concerns with the use of hydrogen, which is required as a fuel for PEMFC, for portable microdevices, such as storage, safety, and refueling. Methanol has been identified as a highly suitable liquid fuel for producing hydrogen because it offers a high hydrogen–carbon ratio, absence of carbon–carbon bonds, potentially high production capacity, and easy handling [1–4]. Methanol must be converted into hydrogen through the reforming reaction to be used as a fuel for PEMFC. Efficient heat transfer is important in the reforming reaction because steam reforming of methanol is a highly endothermic reaction. Compared to large industrial scale reactors, micro-reactors offer advantages of improved heat and mass transfer, more precise control of reaction temperature within flammable

regions leading to reduced hot spots, and higher surface area to volume ratios of micro-channels. As a result, the micro-reactors have been widely used for gas and liquid phase chemical reactions, enzyme reactions, heat exchangers, etc. as the conversion and selectivity for various chemical reactions were improved [4–8]. The micro-reactors have been fabricated with various materials such as stainless steel, Pyrex glass, aluminum plates, polymers, ceramics, and silicon wafers. In this study, a silicon wafer was chosen because of its excellent thermal properties, lower cost, and the ease to scale down by well-established silicon micromachining technologies such as photolithography, wet chemical etching, reactive ion etching, various bonding methods and thin film deposition.

The micro-reactors used for chemical reactions such as methanol steam reforming require a catalyst layer. If the micro-channels of micro-reactors are packed with catalyst particles, as in widely used packed bed reactors, the maximum yield for chemical reaction cannot be expected due to poor heat transfer characteristics, high pressure drop, and possible channeling of reactant gases [9–13]. Therefore, several techniques such as chemical vapor deposition (CVD), physical vapor deposition (PVD), anodic oxidation, sol–gel coating, wash coating, and

* Corresponding author. Tel.: +82 2 880 8863; fax: +82 2 888 7295.

E-mail address: jjkimm@snu.ac.kr (J.J. Kim).

electro-deposition have been used for catalyst coating of micro-reactors. Thin film catalyst layers deposited by PVD and CVD provide lower catalyst surface areas due to smooth catalyst films, and those methods are limited to elemental catalyst composition. Franz et al. introduced a wet catalyst deposition method using aerosols of a metal salt solution to get higher surface areas than PVD or CVD for partial oxidation reactions [14]. Kursawe et al., Liauw et al., and Rebrov et al. selected anodic oxidation of silicon or aluminum plates through electrolysis or thermal oxidation as another way to obtain high surface areas. A catalyst layer was then deposited on the porous surface formed by anodic oxidation using wet impregnation, CVD and wash coating for selective hydrogenation or ammonia oxidation. However, these methods were restricted to the formation of sub-micron layers in porous structures [15–21]. Pfeifer et al., Zapf et al., and Steinfeldt et al. directly coated catalysts on various substrates by wash coating [22–24]. Deposition of porous thin film through sol–gel processes has also been carried out on plates or patterned substrates with the use of dip and spin coating by other groups (Hass-Santo et al., Zhao et al., etc.) [25–28]. Gorges et al., and Kusakabe et al., tested anodic spark deposition and electrolysis methods for catalyst coating [29,30]. However, those coating methods could not be applied to the pre-assembled silicon-based micro-reactors used in this study because the catalyst layer pre-coated on the ribs of micro-channels resulted in air leakage due to incomplete bonding when the patterned silicon wafer was bonded with Pyrex glass to assemble the micro-reactor. Thus, in this study, coating methods for pre-assembled micro-reactors were investigated. Two coating methods with two types of catalyst slurry were utilized to form the catalyst layer on the inner walls of the micro-channels after micro-reactor assembly.

2. Experimental

Silicon-based micro-reactors were fabricated with micro-electro-mechanical systems (MEMS) and silicon micromachining technology. Rectangular micro-channels were etched onto (1 1 0) silicon wafers by anisotropic wet etching with a 30 wt.% KOH solution. The dimensions of micro-channels were 600 μm (width) \times 240 μm (depth) \times 37.5 cm (length). The patterned silicon wafer was bonded to Pyrex by anodic bonding to assemble the micro-reactor. The inner walls of the micro-channels were pre-coated with alumina as an adhesive layer between the catalyst layer and silicon surface with the catalyst layer subsequently coated onto the alumina layer [31].

Alumina sol was prepared by the Yoldas process to form a glue layer [32]. Aluminum isopropoxide ($\text{Al}(\text{OC}_3\text{H}_7)_3$) was hydrolyzed in deionized (DI) water. The solution was then vigorously stirred for 1 h at 80–92 °C for complete mixing and hydrolysis. Hydrogen chloride (HCl) was added to peptize the alumina sol and to adjust the pH. Polyvinyl alcohol (PVA) was added as a drying control chemical additive to reduce crack formation of the alumina layer and improve adhesion between the alumina layer and the silicon substrate during drying and

calcinations [33,34]. The PVA solution was prepared by dissolving PVA in DI water at 80–90 °C. The prepared alumina sol and PVA solution were mixed by stirring for 1 h. Thermogravimetric analysis (TGA) was conducted to confirm the reducing effect of evaporation rate by PVA addition in alumina sol.

A commercial Cu–ZnO–Al₂O₃ catalyst from Süd-Chemie (MDC-3) was used as the reforming catalyst in all experiments for steam reforming of methanol at the relatively low temperature of 250–300 °C [35–38]. Catalyst slurries were prepared by ball milling for 5 days. Two types of catalyst slurries were made with either alumina sol or DI water as the solvent of catalyst slurry. The catalyst slurries were named alumina sol-based slurry and DI water-based slurry. The viscosity of catalyst slurries was adjusted by changing the ratio of catalyst to solvent.

Dip coating tests were initially performed on (1 1 0) bare silicon to investigate the minimum thickness of alumina layer required for catalyst coating as well as the effects of PVA addition. Bare and patterned wafers were immersed into alumina sol or catalyst slurry and then pulled vertically from the coating solution at a constant drawing speed. Alumina layers of various thicknesses were made by adjusting the drawing speed of the wafer from the coating solution. Catalyst was then coated onto the alumina layers of various thicknesses in order to determine the minimum thickness of alumina layer required for catalyst coating.

Based on the critical thickness and the effects of PVA addition, alumina sol was coated on the inner walls of micro-channels by a flow coating method. The micro-channels were filled with alumina sol and then non-adsorbed alumina sol was removed by air flowing. The coated micro-channels were then dried at room temperature and calcined at 500 °C for 3 h. The effects of the air flow rate and alumina sol residence time on alumina layer thickness were also examined.

Two methods, flow coating and fill-and-dry coating, were used to deposit the catalyst layer. In the case of flow coating, micro-channels pre-coated with an alumina adhesive layer were filled with the catalyst slurry, followed by the removal of surplus slurry by air flowing. The coated micro-channels were then dried at room temperature for a day and calcined at 300 °C for 3 h. In the fill-and-dry coating technique, the micro-channels filled with the catalyst slurry underwent the room temperature drying and calcinations at 300 °C without removing excess slurry by air flowing.

The cross-sectional morphologies as well as the thicknesses of alumina and catalyst layers coated onto the micro-channels were examined using a field emission scanning electron microscope (FESEM). The viscosity of the catalyst slurry was measured with a rheometer (Bohlin Instrument). The adhesion of alumina as an adhesion layer was tested on the bare wafer by the American Society for Testing and Materials Standard Test Method for Film Adhesion by Tape Test (ASTM D 3359).

Micro-reformer stacks composed with one vaporizer to evaporate the methanol solution and two micro-reformers were fabricated using stainless steel end plates in order to compare the activity of catalyst made by different coating methods and

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