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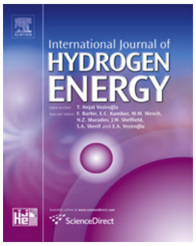

Technical Communication

Hydrogen production from ethanol over Co/ZnO catalyst in a multi-layered reformer

Yong-Kul Lee[a,*], Kyoung-Suk Kim[a], Jin-Goo Ahn[b], In-Hyuk Son[b], Woo Cheol Shin[b]

[a] Laboratory of Advanced Catalysis for Energy and Environment, Department of Chemical Engineering, Dankook University, 126 Jukjeondong, Yongin 448-701, South Korea
[b] Energy Laboratory, Samsung SDI, Suwon 443-391, South Korea

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ABSTRACT

A Co/ZnO catalyst was prepared by coprecipitation method, and was applied for ethanol steam reforming. The effect of reaction conditions on the ethanol steam reforming performance was studied in the temperature ranges from 400 °C to 600 °C and the space velocity ranges from 10,000 h^{-1} to 120,000 h^{-1} in a fixed bed reactor. The Co/ZnO showed high activity with an ethanol conversion of 97% and a H_2 concentration of 73% at a gas hourly space velocity of 40,000 h^{-1} and a moderately low temperature of 450 °C. EXAFS analysis for fresh and spent samples confirms that Co phase maintains during reaction. The catalyst was then loaded into a multi-layered reformer of which the design concept allows for integrating endothermic steam reforming, exothermic combustion and evaporation in a reactor. The performance of the compact reformer demonstrated that the hydrogen production rate satisfy a PEMFC stack power level of 540 W suitable for portable power supplies.

1. Introduction

Recent advances in the polymer electrolyte membrane fuel cell (PEMFC) have driven much interest in the area of vehicle, residential and portable power supplies. For a small sized fuel cell system for portable applications efficient, light and safe hydrogen carriers are needed since the direct use of hydrogen in the form of a compressed vessel or a metal hydride could increase the total system volume or weight. As a result, much attention has been made to convert readily available fuels to hydrogen. The conversion of commercial fuels like hydrocarbon and alcohol to hydrogen can be achieved by catalytic chemical reactions such as steam reforming, partial oxidation and autothermal reforming [1,2]. In general alcohol fuels like methanol and ethanol are more reactive than hydrocarbon fuels for steam reforming and are thus converted to hydrogen at lower temperature ranges than the cases of hydrocarbon reforming which occurs above 700 °C.

This study focuses on the ethanol steam reforming over an transition metal catalyst in a multi-layered reformer for portable fuel cell system applications, since it can be easily converted to hydrogen by steam reforming and be renewably produced from biomass [3]. Among catalysts active for steam reforming, precious metals such as Rh, Rt, Pd, and Ru are known to be active for ethanol steam reforming, but they require relatively high reaction temperatures above 600 °C [4–8,11–13]. The high reaction temperature would increase the reactor volume due to an additional insulation and result in the

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[*] *Corresponding author*. Tel.: +82 31 8005 3466; fax: +82 31 8005 3536.
E-mail address: yolee@dankook.ac.kr (Y.-K. Lee).

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Table 1 – Physical properties of Co/ZnO sample.

	Composition (wt.%)	BET surface area ($m^2\ g^{-1}$)
Co/ZnO catalyst	1.1% Na 10.3% Co 88.6% Zn	13

increase of CO levels in the product stream due to the reverse water gas shift reaction being favored. Thus, in this study Co/ZnO catalyst was chosen for ethanol steam reforming, because it is one of the most active transition metal oxide for the reaction [9,10]. The catalytic activity was measured at wide temperature ranges from 400 to 600 °C and at atmospheric pressure in a fixed bed reactor for steam reforming using a model feed liquid of ethanol aqueous solution. The effect of space velocity on the catalytic performance was also examined with varying catalyst loadings and feed flow rates. This study also includes the possible use of Co/ZnO catalyst in the multi-layered compact reformer for portable fuel cell system.

2. Experimental

Catalysts were prepared by the coprecipitation method. An aqueous solution of $Zn(NO_3)_2$ $6H_2O$(99%, Aldrich), $Co(NO_3)_2$ $6H_2O$ (99%, Aldrich) was precipitated by the addition of a Na_2CO_3 (99%, Aldrich) solution at 50 °C under continuous stirring. After aging at 50 °C for 1.5 h, the resulting precipitate was filtered out. The cake collected from the precipitate was dried at 120 °C overnight and calcined under air flow at 500 °C for 5 h, which was then palletized under a pressure of 3.0×10^8 Pa to give uniform 1.0 mm pellets. The elemental analysis on the catalyst sample made by ICP-AES is listed in Table 1. The active phase in the catalyst was examined using extended X-ray absorption fine structure (EXAFS) spectra, measured at the 3C-1 beamline in Pohang Accelerator Laboratory with a 2.5 GeV ring energy and a 200 mA ring current. The fresh sample was pretreated in H_2 flow at 450 °C and transferred to an aluminum cell with Kapton windows. The spent sample was taken from the reactor, washed with hexane, and then pretreated in He flow at 340 °C without exposure to air and similarly transferred to an aluminum cell. For the EXAFS analysis comparisons were made with Co foil.

Catalytic studies of ethanol steam reforming were carried out at atmospheric pressure with varying temperatures from 400 to 600 °C in a conventional fixed bed reactor (SUS304, 8 mm internal diameter). The feed liquid was prepared by mixing 20% ethanol (Aldrich, 99.99%) and 80% distilled water by volume, and was delivered to the reactor by a liquid pump (LabAlliance Series1) through a vaporizer heated to 400 °C. The catalytic performance was measured at every 50 °C step up to 600 °C. Quantities of catalysts loaded in the reactor and flow rates of feed liquid were varied corresponding to gas hourly space velocities (GHSV) of 10,000–120,000 h^{-1}. Gas product compositions were determined with a gas analyzer (Emerson,

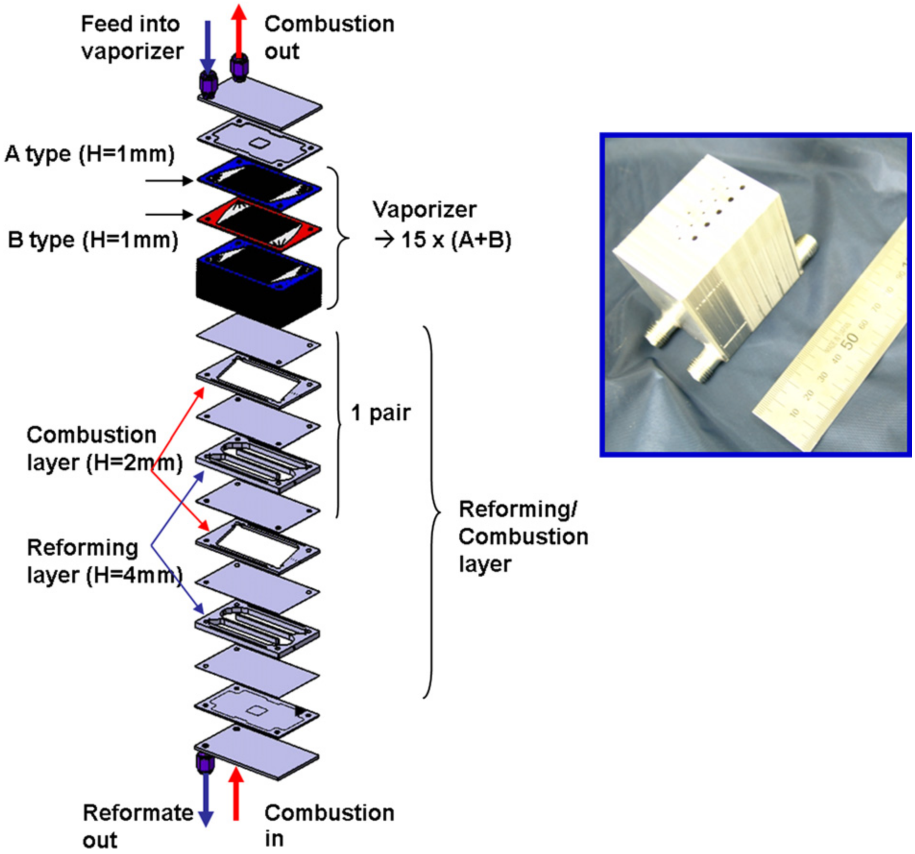

Fig. 1 – Schematic diagram of muti-layered reformer.