Available online at www.sciencedirect.com

ScienceDirect

Journal of Energy Chemistry 22(2013)861–868

JOURNAL OF ENERGY CHEMISTRY

www.elsevier.com/locate/jngc

Low CO content hydrogen production from oxidative steam reforming of ethanol over $CuO-CeO_2$ catalysts at low-temperature

Xue Han, Yunbo Yu, Hong He*, Jiaojiao Zhao

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, China

[Manuscript received February 25, 2013; revised April 18, 2013]

Abstract

$CuO-CeO_2$ catalysts were prepared by a urea precipitation method for the oxidative steam reforming of ethanol at low-temperature. The catalytic performance was evaluated and the catalysts were characterized by inductively coupled plasma atomic emission spectroscopy, X-ray diffraction, temperature-programmed reduction, field emission scanning electron microscopy and thermo-gravimetric analysis. Over $CuO-CeO_2$ catalysts, H_2 with low CO content was produced in the whole tested temperature range of 250–450 °C. The non-noble metal catalyst 20CuCe showed higher H_2 production rate than 1%Rh/CeO_2 catalyst at 300–400 °C and the advantage was more obvious after 20 h testing at 400 °C. These results further confirmed that $CuO-CeO_2$ catalysts may be suitable candidates for low temperature hydrogen production from ethanol.

Key words

$CuO-CeO_2$ catalyst; hydrogen production; oxidative steam reforming; low-temperature

1. Introduction

Ethanol is an important candidate as a chemical carrier of hydrogen, the production of which is useful in a series of fuel cell applications [1–3]. Not only is it less hazardous than methanol, but it can be produced from a variety of biomass sources [4–6]. A typical fuel processor is made up of different processing units such as fuel reformers and CO cleanup reactors. CO cleanup is essential for fuel processor, since the electrodes can only tolerate about 1%–2% CO for phosphoric acid fuel cell (PAFC) and less than 10 ppm for proton exchange membrane fuel cell (PEMFC) [7]. PEMFC and PAFC are classified as low-temperature fuel cells, suitable for automotive applications, operating in the ranges of 80–120 °C and 180–220 °C, respectively. Therefore, if low CO content hydrogen can be produced at low temperatures, this can in turn lower the cost and size of fuel cells by reducing or eliminating the stacks of CO cleanup processing units.

Typical routes for hydrogen production from ethanol are shown in the following equations: steam reforming (SR, Equation 1), partial oxidation (PO, Equation 2), and oxidative steam reforming (OSR, Equation 3).

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{1}$$

$$C_2H_5OH + 1.5O_2 \rightarrow 2CO_2 + 3H_2 \tag{2}$$

$$C_2H_5OH + (3-2x)\,H_2O + xO_2 \rightarrow 2CO_2 + (6-2x)\,H_2 \quad (0 < x \leqslant 0.5) \tag{3}$$

The SR of ethanol provides high hydrogen selectivity, however, it is a highly endothermic reaction, typically operating within the temperature range of 450–700 °C even with the help of catalysts [8,9]. The high reforming temperature also favors the reverse water-gas shift (R-WGS) reaction (CO_2+H_2→CO+H_2O) and thus the generation of CO, the presence of which degrades the performance of Pt electrodes in fuel cell systems [7]. In contrast, the PO of ethanol is an exothermic reaction, the operation temperature of which can be greatly lowered over suitable catalysts. In this case, however, its hydrogen selectivity is decreased [1]. The OSR of ethanol combines both the SR and PO reactions. This means that high hydrogen selectivity can be achieved at low temperatures under OSR conditions with suitable reaction conditions and choice of catalyst.

Ni, Co, Cu and noble metals are common active components which are frequently studied for hydrogen production by steam reforming [10–13]. Although supported noble metal

---

* Corresponding author. Tel: +86-10-62849123; Fax: +86-10-62849123; E-mail: honghe@rcees.ac.cn

This work was supported by the National Basic Research Program of China (2010CB732304) and the National Natural Science Foundation of China (21177142 and 20973193).

catalysts, specially Rh, have been demonstrated to exhibit significant activity at low temperatures and high space velocities, the high cost of these metals limits their application [13]. CeO_2 has been extensively utilized as a support for OSR of ethanol mainly due to its remarkable oxygen-storage/release capacity (OSC) and high oxygen mobility, allowing gasification/oxidation of deposited carbon as soon as it forms, and thus improving the catalyst stability [2,9]. Meanwhile, CeO_2 favors ethanol dehydrogenation to acetaldehyde rather than dehydration to ethylene, which is easily polymerizable to coke [14,15]. Furthermore, CuO-CeO_2 catalysts have good activity for the oxidation of CO in a hydrogen-rich stream [16] and their catalytic performance for hydrogen production from SR of ethanol has been reported [13]. Inspired by all of the above, we employed CuO-CeO_2 mixed oxide as a catalyst for OSR reaction for the first time.

It has been extensively reported that CuO-CeO_2 materials can be prepared by hydrothermal treatments [17,18], a hard template method [13] and combustion method [19–21]. However, the former two methods are complicated and the combustion method tends to lead to low surface area. In this work, CuO-CeO_2 catalysts with varying Cu/(Cu+Ce) mole ratio were prepared by urea co-precipitation, which is a homogeneous precipitation method, characterized by a highly uniform increase in pH value of metal salts solution. It is a convenient method for catalyst preparation that can produce highly dispersed mixed metal oxides [22]. The H_2 yield rate and product distribution of CuO-CeO_2 catalysts under OSR conditions with high space velocity were tested and compared with 1%Rh/CeO_2 catalyst.

2. Experimental

2.1. Catalyst preparation

CeO_2 and CuO-CeO_2 mixed oxides catalysts with nominal CuO contents of 10, 20, 30 and 40 mol% were synthesized by a urea precipitation method. Appropriate amounts of copper (II) nitrate hexahydrate ($Cu(NO_3)_2{\cdot}3H_2O$, 99%) and cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, 99%) were dissolved in water together with urea, and the metal ion concentration (Cu+Ce) was fixed at 0.5 mol/L. After stirring for 24 h at 90 °C, the precipitate was dried at 100 °C for 12 h, and then thermally treated in a furnace at 500 °C for 5 h in air. CuO-CeO_2 mixed oxides catalysts were expressed as mCuCe, where m is the nominal CuO content. For comparison, a CeO_2-supported Rh catalyst was also prepared by an impregnation method, followed by drying at 100 °C for 12 h and calcination at 500 °C for 3 h in air. Rhodium loading was fixed at 1 wt% and the precursor was $RhCl_3{\cdot}3H_2O$. This CeO_2-supported Rh catalyst was expressed as 1%Rh/Ce.

2.2. Catalyst characterization

The BET surface area, average pore diameter and total pore volume of catalysts were determined on Autosorb iQ-1MP automatic equipment by physical adsorption measurement with N_2 at –196 °C. Prior to N_2 physical sorption, the samples were degassed.

The chemical composition of the catalyst was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an OPTIMA 2000DV spectrometer.

X-ray powder diffraction (XRD) patterns were measured using a PANalytical X'Pert Pro diffractometer with Cu K_α ($\lambda = 0.15406$ nm) radiation. The data were collected for 2θ from 10° to 90° at 6 °/min with a step size of 0.026°.

The surface morphologies of fresh and used catalysts were studied by SU-8020 field emission scanning electron microscopy (FE-SEM). Powder samples were mounted directly on aluminum sample holders and placed in SEM chamber without gold sputter coating.

Hydrogen temperature-programmed reduction (H_2-TPR) measurements were carried out in a conventional set-up equipped with a thermal conductivity detector (TCD). Samples (200 mg) were heated from room temperature to 800 °C in a reducing gas mixture (10 vol% H_2/He, 50 $mL{\cdot}min^{-1}$) at a ramp rate of 10 $°C{\cdot}min^{-1}$.

The carbon deposition rates over catalysts during OSR reaction were measured by thermo-gravimetric analysis (TGA, STARe system METTLER TOLEDO) method. The aged catalyst were heated in pure O_2 (50 $mL{\cdot}min^{-1}$) from 30 to 900 °C at a heating rate of 20 $°C{\cdot}min^{-1}$. Simultaneously, the weight change of the employed catalyst was measured with time on-stream.

2.3. Catalytic test

The OSR reaction of ethanol was carried out in a continuous-flow fixed-bed microreactor made of a quartz tube of 6 mm in inner diameter with 100±2 mg catalyst (40–60 mesh, diluted with 300 mg SiO_2). A mixture of ethanol and water was supplied by a syringe pump at a rate of 0.06 $mL{\cdot}min^{-1}$. After being sufficiently vaporized by passing through a preheating zone at 150 °C, this mixture was continuously fed into the reactor together with N_2 carrier and O_2 (EtOH : H_2O : O_2 = 1 : 3 : 0.5), with a mixed gas flow rate of 350 $mL{\cdot}min^{-1}$. The reaction temperature (measured with a thermocouple located in the middle of the catalyst bed) was increased in 25 °C increments from 250 to 450 °C, and each temperature point was maintained for at least 1 h. The liquid products were removed by condensation and then the effluent gases were analyzed on-line at each temperature point using a gas chromatograph (Shimadzu, GC-2014C) equipped with two TCDs and one FID. The TCDs detection limits of N_2, H_2, CO, CO_2 and CH_4 products were 200 ppm.

Since this work was carried out at on-board conditions, a room temperature normal flow rate (F_x) that takes the volume change into account was considered to calculate H_2 yield rate and product distribution:

$$F_x = \frac{[X] \times F_{N_2}}{[N_2]} \qquad (4)$$

where, F_{N_2} is the N_2 flow rate at room temperature, [N_2] is