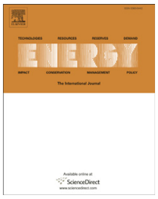
Energy xxx (2014) 1–9

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy



Modified oxalic acid co-precipitation method for preparing $Cu/ZnO/Al_2O_3/Cr_2O_3/CeO_2$ catalysts for the OR (oxidative reforming) of M (methanol) to produce H_2 (hydrogen) gas

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ARTICLE INFO

Article history:
Received 8 July 2013
Received in revised form
28 January 2014
Accepted 18 March 2014
Available online xxx

Keywords:
Oxidative
Reforming
M (methanol)
H_2 (hydrogen)
Catalyst
Oxalic co-precipitation

ABSTRACT

OR (oxidative reforming) of M (methanol) was performed using $Cu/ZnO/Al_2O_3$-based catalysts, prepared using an oxalic co-precipitation method. We optimized the active catalyst formulation for low reaction temperatures and investigated the effects of varying the steam–methanol mole ratio, the oxygen–methanol mole ratio, WHSV (weight hourly space velocity), precursor mix formulation, reaction temperature, and precipitation temperature, pH, and DTs (drying times) of oxalic acid co-precipitated precursors. The $Cu/ZnO/Al_2O_3/Cr_2O_3/CeO_2$ (15/15/2.5/1.25/1.25) catalyst provided greater than 80% conversion to methanol at 200 °C under CO (carbon monoxide) at 900 ppm, and provided a 100-h lifetime.

1. Introduction

Hydrogen gas has potential as a fuel for producing electrical energy in electric vehicles and plant [1,2]. Hydrogen-powered fuel cells are well established; however, an infrastructure for the distribution and supply of hydrogen gas is not so well developed. Thus, in the short to medium term, onboard catalytic generation of hydrogen from liquids or liquefied fuels may provide a solution to this issue [3].

Designing fuel reforming systems involves numerous considerations [4–7]. CO (carbon monoxide) is a poison for PEMFC (polymer electrolyte-membrane fuel cells), thus, CO concentrations must minimized, typically to less than 10 ppm [8]. Kahlich et al. [9] reported that when using a 0.5% Pt/Al_2O_3 catalyst, CO concentrations were substantially reduced at reaction temperatures greater than 200 °C [9]. Mariño et al. [10] reported that including Co, Cr, Cu, Ni, or Zn in the catalyst could reduce CO concentrations, and found that a $Cu-CeO_2$ catalyst yielded the greatest reduction in CO concentration. Specifically, this catalyst reduced the concentration of CO from 20,000 ppm to 325 ppm at 157 °C [10]. Moreover, the high temperature PEMFC with phosphoric acid doped polybenzimidazole was reported high conductivity, good thermal stability and good fuel cell performance at temperature up to 200 °C. The affinity for CO onto the platinum catalyst is reduced and CO tolerance is increased (e.g., above 160 °C upto 3% CO can be tolerated in the fuel stream). This offers a significant advantage to fuel processing and gascleaning can be removed thus allowing for cost-effective fuel [11].

Using an appropriate catalyst offers the advantage of producing hydrogen gas with relatively low CO content during M (methanol) reforming [12]. Methanol OSR (oxidative steam reforming) catalysts are based on $Cu/ZnO/Al_2O_3$-oxides, and are similar to the catalyst systems used for SRM (steam reforming methanol). $Cu/ZnO/Al_2O_3$-oxides provide favorable reforming activities after a complete reduction pre-treatment. Deactivating copper-based catalysts present a formidable obstacle for their technical implementation; however, modification with ZrO_2, Cr_2O_3, CeO_2, or TiO_2 can provide improvements in catalytic activity [13]. In this study, CeO_2 and Cr_2O_3 were incorporated into the Cu-based catalyst.

Hydrogen can be produced from methanol by using various catalytic processes: SRM (Eq. (1)), POM (partial oxidation methanol) (Eq. (2)), and OSRM (oxidative steam reforming methanol) also called OR (oxidative reforming), which is a combination of SRM and POM [14].

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http://dx.doi.org/10.1016/j.energy.2014.03.073
0360-5442/

Please cite this article in press as: Lesmana D, Wu H-S, Modified oxalic acid co-precipitation method for preparing $Cu/ZnO/Al_2O_3/Cr_2O_3/CeO_2$ catalysts for the OR (oxidative reforming) of M (methanol) to produce H_2 (hydrogen) gas, Energy (2014), http://dx.doi.org/10.1016/j.energy.2014.03.073

$$CH_3OH_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + 3H_{2(g)} (\Delta H = +49.5 \text{kJ/mol}) \quad (1)$$

$$CH_3OH_{(g)} + 0.5O_{2(g)} \rightarrow CO_{2(g)} + 2H_{2(g)} (\Delta H = -192.2 \text{kJ/mol}) \quad (2)$$

The OSRM process combines endothermic Eq. (1) with exothermic Eq. (2) in a reactor. OSRM does not require an external heat supply, and produces a reasonable H_2 concentration (65%) using air as the oxidant supply. Compared with SRM, OSRM systems offer advantages of a simpler reactor design with smaller volume [14].

The objective of this study was to identify active catalysts for low-temperature methanol reforming to produce hydrogen, while minimizing CO production. The effects of using Cr_2O_3 and CeO_2 promoted $Cu/Zn/Al_2O_3$ catalysts, the precipitation pH value, the precursor precipitation DT (drying time), the precursor mix formulation, and the reaction temperature were studied.

2. Experimental

2.1. Materials

Methanol (99%, Mallinckrodt, USA), copper nitrate-2.5-hydrate (99%, R.D.H, Germany), zincnitrate-6-hydrate (99%, R.D.H, Germany), aluminum nitrate-9-hydrate (99%, J.T. Baker, USA), chromium nitrate-6-hydrate (99%, R.D.H, Germany), cerium nitrate-6-hydrate (99%, R.D.H, Germany), oxalic acid (99%, R.D.H, Germany), HiFuel™ R120 catalyst (copper-based methanol reforming catalyst pellets, 5.2 × 3.0 mm, Alfa Aesar, UK). The HiFuel™ R120 catalyst was milled and sieved to provide 60–80 mesh particles by using a sieve shaker. All other reagents were used as supplied.

2.2. Preparing catalysts

Catalyst precursor solutions were prepared by introducing each of $Cu(NO_3)_2 \cdot 2.5H_2O_{(s)}$, $Zn(NO_3)_2 \cdot 6H_2O_{(s)}$, $Al(NO_3)_3 \cdot 9H_2O_{(s)}$, $Cr(NO_3)_2 \cdot 6H_2O_{(s)}$, and $Ce(NO_3)_3 \cdot 6H_2O_{(s)}$ into flasks containing ethanol (100 mL) at −5 °C, to concentration of 1 mol/L, and stirring the solutions until dissolved. Each precursor solution was reacted with 20% excess oxalic acid. The precursor and oxalic acid solutions were divided into three types for optimizing catalytic activity (Fig. 1). Type B precursors underwent conventional mixing during oxalic co-precipitation [15]. Type A and type C used modified mixing methods.

Aqueous ammonia (approx. 25%) was added to the precursor and oxalic acid solutions, to adjust pH from an approximately pH 0.4–1.0, using a pH meter (SP-701, Suntex, Taiwan). The as-formed precipitate was filtered and washed with deionized water, and then dried at 100 °C for various times, in the range 18–27 h. All precursors were then calcined under O_2 at a flow rate of 100 mL/min, by applying a programmed temperature regime [15] as follows:

$$\text{RT} \xrightarrow{30\text{ min}} 150\,^\circ\text{C} \xrightarrow{25\text{ min}^*} 150\,^\circ\text{C} \xrightarrow{20\text{ min}} 200\,^\circ\text{C} \xrightarrow{25\text{ min}^*} 200\,^\circ\text{C}$$
$$\xrightarrow{20\text{ min}} 250\,^\circ\text{C} \xrightarrow{25\text{ min}^*} 250\,^\circ\text{C} \xrightarrow{20\text{ min}} 300\,^\circ\text{C} \xrightarrow{3\text{ h}^*} 300\,^\circ\text{C}$$

in which the time marked with "*" is holding time, and the others are heating time.

After calcination, the precipitates were ground into granules, and 60–80 mesh particles were separated and collected by sieving. The catalyst materials were then reduced in a stream of 10% H_2/N_2 at a flow rate of 100 mL/min, and at an initial temperature of 25 °C and final temperature of 300 °C at a heating rate of 5 °C/min for 3 h.

Catalytic properties were characterized using a chemBET TPR (temperature-programmed reduction)/TPD chemisorption analyzer (Quantachrome Instruments, USA) to determine the reproducibility of the fresh catalysts. Next, 0.1 g of sample was placed in a quartz fixed bed reactor, and a high-purity flow of 10 vol % H_2–Ar mixture (TPR) was passed through the bed at 30 mL/min. The sample temperature was increased at a rate of 5 °C/min from 30 °C to 400 °C, and the composition of hydrogen was monitored using GC (gas chromatography) (Shimadzu 8A, Japan) using a TCD (thermal conductivity detector) cell, and recorded onto a computer.

A SEM (scanning electron microscope) (Hitch 2460N, Japan) with EDX (energy dispersive X-ray spectrometer) (INCA, Oxford Instruments, Oxford, United Kingdom) was used to determine the morphology of the catalyst surface; catalysts were compressed into a tablet and placed into the sample processor, and then decompressed using a turbo pump system to 2×10^{-6} kPa. Finally, the gate separating the sample processor and vacuum chamber was opened, and the sample then moved into the vacuum chamber for analysis. SEM operating parameters for wide scan were dw = 0.05 S, DPI (dot per inch) = 1 eV, Scan number = 50, Scan range = 0–1200 eV. The

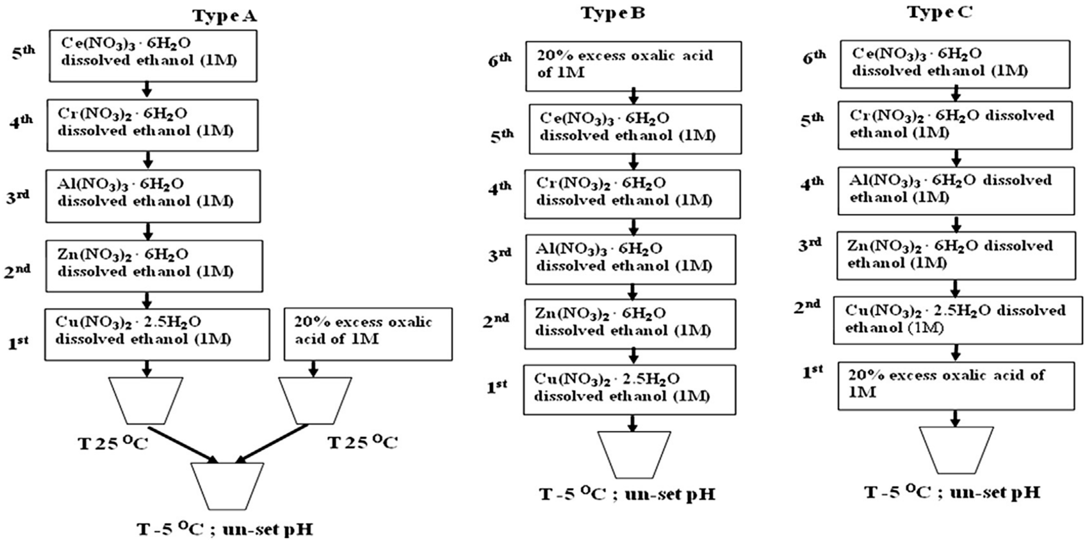

Fig. 1. Types of mixing of precursor catalysts.

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