INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–16

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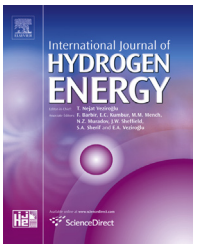

Hydrogen production with a low carbon monoxide content via methanol steam reforming over $Cu_xCe_yMg_z/Al_2O_3$ catalysts: Optimization and stability

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ARTICLE INFO

Article history:
Received 27 December 2016
Received in revised form
16 March 2017
Accepted 20 March 2017
Available online xxx

Keywords:
Hydrogen production
CO selectivity
Methanol steam reforming
Copper catalysts
Ceria–magnesium oxide bi-promoter

ABSTRACT

Catalytic activities of Ce–Mg promoted Cu/Al_2O_3 catalysts via methanol steam reforming was investigated in terms of the methanol conversion level, carbon monoxide selectivity and hydrogen yield. The factors chosen were the reaction temperature, copper content, Mg/(Ce + Mg) weight-percentage and steam to carbon ratios. The catalysts were prepared by co-precipitation and characterized by means of XRD, BET, H_2-TPR, and FESEM. The Ce–Mg bi-promoter catalysts gave higher performance due to magnesium penetration into the cerium structure causing oxygen vacancy defects on the ceria. A response-surface-model was then designed to optimize the condition at a 95% confidence interval for complete methanol conversion to a high H_2 yield with a low CO content, and revealed an optimal copper level of 46–50 wt%, Mg/(Ce + Mg) of 16.2–18.0%, temperature of 245–250 °C and S/C ratio of 1.74–1.80. No deactivation of the $Cu_{0.5}Ce_{0.25}Mg_{0.05}/Al$ catalyst was observed during a 72-h stability test.

Introduction

The increasing global human population with increasing industrialization and economic development is driving a rapid growth in energy consumption, yet the global primary fuel supply is, in contrast, decreasing leading towards a shortfall in the future. Indeed, around 85% of the global energy supply is derived from fossil fuel [1–4], which is non-renewable and limited in nature and so the prospect of an energy supply shortage has become more serious. Along with fossil fuel utilization, the increase in global economic growth with attained wealth has raised the standard of living and increased the quality of life at the cost of increased energy

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http://dx.doi.org/10.1016/j.ijhydene.2017.03.112
0360-3199/

consumption, and this threatens the environment from, for example, the emission of pollutants, especially greenhouse gases that are potentially a major cause of global warming. One of the tactics to overcome these troubles is to reduce the dependence on fossil fuels and seek out a friendly alternative renewable energy. Hydrogen (H_2) is one of the most promising carbon-free clean energy carriers, where H_2 oxidation produces only steam and heat. There are various methods to produce H_2, depending on the type of feedstock, such as splitting water by electrolysis, gasification of biomass, steam reforming of hydrocarbons, etc. Even though water seems to be an interesting feedstock, it is not suitable as long as populations face a lack of consumable water resources. However, H_2 production from biomass-derived oxygenated hydrocarbons by catalytic reforming has recently been developed [2–6]. This method produces a H_2-rich stream at moderate reaction temperatures (200–300 °C). Alcohols, like methanol (CH_3OH), have received a lot of attention since methanol is readily available and can be produced from renewable sources. Moreover, methanol has a high density that allows it to be stored, transported and applied in a conventional infrastructure. The high hydrogen to carbon ratio and an absence of C–C bonds in the methanol structure lead to minimal coke formation on the catalyst. No auxiliary unit, such as desulfurization and pre-reforming processes, is required when catalytically converting methanol to a H_2-rich stream. From the stoichiometry of the overall reaction for methanol steam reforming (MSR), as shown in Eq. (1), no carbon monoxide (CO) is produced in the H_2-rich stream,

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (1)$$

However, in fact around 1–10% (v/v) CO is found in the reformed gaseous effluent, which has led to the proposal that MSR is comprised of the two-sequential reactions of methanol decomposition (MD) and the water-gas shift (WGS) reaction of CO [4,5,7–17]. The methanol first decomposes to CO and H_2 in the MD reaction, and then the CO reacts with steam to produce carbon dioxide (CO_2) and H_2 in the WGS reaction. However, a lower H_2 yield is obtained at higher operating temperatures (350–450 °C) since the reverse WGS reaction occurs. Therefore, attempts to improve the catalyst performance at lower temperatures have become a significant key in the development of MSR, where a MSR catalyst with a high methanol conversion level to yield H_2-rich stream with a low CO content is required.

Noble metal and copper-based catalysts have been widely used for MSR [4,7–27]. Even though noble metal catalysts give a good performance, their cost is quite high and they are potentially deactivated due to their low CO tolerance [5]. Copper-based catalysts, especially $CuO/ZnO/Al_2O_3$ commercial catalysts, have a good performance because of their high catalytic activity. However, there are many concerns about the sintering of active copper that leads to its deactivation [14]. Alumina is often used as a support for copper-based catalysts because of its chemical stability and high surface area [25–27]. Nevertheless, the acidic property of the alumina support encourages coke formation [5,9,10,18], resulting in a declined catalytic performance. Thus, promoters supported on the alumina surface are required to reduce the coke formation and so improve the catalytic performance. Some research reported that the acidity of alumina could be neutralized with magnesium oxide (MgO) [11,12,22]. Moreover, the use of cerium oxide (CeO_2), or ceria, as a promoter for MSR catalysts has attracted considerable recent attention due to its high level of oxygen vacancies, which are crucial to promote the stability and enhance the catalytic performance [8–10]. It has been proposed that $CuO\text{-}CeO_2$ catalysts exhibit a higher catalytic performance than commercial catalysts due to their improved ability to transfer bulk oxygen in CeO_2 to its surface [12,16,18]. Many works have studied the catalytic performance based on single promoters at a time, but the synergistic effect of two different types of promoter, and in particular a Ce–Mg bi-promoter, has largely been neglected. Moreover, the previous studies have been based on univariate experimental approaches, where any significant interactions among the factors are ignored and important factors are potentially concealed. In practice, it is necessary to identify the critical factors and to adjust these factors in accordance with the levels of the other factors to approach the optimal MSR condition.

Herein, in order to optimize the conditions for maximal methanol conversion with a high H_2 yield and a low CO content, a series of Ce–Mg promoted Cu/Al_2O_3 catalysts was then used in MSR. Firstly, the catalytic performance was investigated by varying the operating temperature, ratios of steam to carbon (S/C ratio), Mg/(Ce + Mg) weight percent (wt%), and amount of Cu loading. Comparison of the performance of the Ce- or Mg- mono-promoted Cu/Al_2O_3 catalysts with that of Ce–Mg bi-promoted Cu/Al_2O_3 catalysts was also performed. The catalytic performance was reported in terms of the methanol conversion level, CO selectivity and H_2 yield. In the second aspect, the optimal condition was also evaluated via a face-centered central composite design response surface model (FCCCD-RSM) based on the two levels of four main factors and their interactions with five central points. All experiments were performed in triplicate and reported as the average. Since an effective catalyst should have not only a high performance but also a good durability, the catalyst with the highest performance at the optimal condition was selected to study its stability over a 72-h reaction period. The catalysts were prepared by co-precipitation and characterized by means of X-ray powder diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area, H_2-temperature-programmed reduction (TPR), and field emission scanning electron microscope (FESEM).

Experimental

Catalyst preparation

Copper-based catalysts supported on alumina with mono- or bi-promoters were prepared by co-precipitation. The level of copper was varied from 20 to 50 wt%, maintaining the total weight of mono- and bi-promoters at 30 wt%. The Ce:Mg weight ratios were designed at 30:0, 25:5, 20:10, 15:15 and 0:30, respectively, to obtain a Mg/(Ce + Mg) wt% of 0, 16.67, 33.33, 50 and 100, respectively. To fabricate the catalysts, the desired

Please cite this article in press as: Phongboonchoo Y, et al., Hydrogen production with a low carbon monoxide content via methanol steam reforming over $Cu_xCe_yMg_z/Al_2O_3$ catalysts: Optimization and stability, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.03.112