

Steam reforming of methanol over CuO/ZnO/CeO₂/ZrO₂/Al₂O₃ catalysts

Gang Huang^a, Biing-Jye Liaw^b, Cheng-Jyun Jhang^a, Yin-Zu Chen^{a,*}

^a Department of Chemical and Materials Engineering, National Central University, Jhongli 32001, Taiwan, ROC

^b Department of Chemical and Materials Engineering, Nanya Institute of Technology, Jhongli 32091, Taiwan, ROC

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ABSTRACT

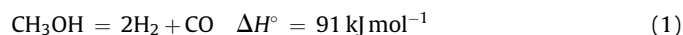
The composition (CuO/ZnO/Al₂O₃ = 30/60/10) of a commercial catalyst G66B was used as a reference for designing CuO/ZnO/CeO₂/ZrO₂/Al₂O₃ catalysts for the steam reforming of methanol (SRM). The effects of ZnO, CeO₂, ZrO₂ and Al₂O₃ on the SRM reaction were clearly identified. CeO₂, ZrO₂ and Al₂O₃ all improved the dispersions of CuO and ZnO in CuO/ZnO/CeO₂/ZrO₂/Al₂O₃ catalysts. Zirconium oxide promoted the SRM reaction and slightly reduced the concentration of CO, but CeO₂ and Al₂O₃ weakened the SRM reaction. The introduction of ZrO₂ into CuO/ZnO/Al₂O₃ (30/60/10) improved the reducibility and stability of the catalyst. The addition of CeO₂ or Al₂O₃ hindered the reducibility of the catalyst and weakened the interaction between CuO and ZnO. Nevertheless, an appropriate amount of Al₂O₃ was needed for the stability and the mechanical strength of the catalysts. The CuO/ZnO/ZrO₂/Al₂O₃ (30/40/20/10) and CuO/ZnO/ZrO₂/Al₂O₃ (40/30/20/10) catalysts are good candidates for the SRM, as determined by comparison with the commercial catalyst G66B.

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1. Introduction

Earlier studies have paid considerable attention to the reduction of hazardous emissions from mobile sources [1,2]. Proton-exchange membrane fuel cells (PEMFC) are being actively considered [3,4]. Combustion in a fuel cell is regarded as a clean process, releasing energy and providing only water as the exhaust material [2,5]. Pure hydrogen is a superior feed for PEMFC, but the supply and the storage of hydrogen raise mechanical and safety problems [1,2,5]. Therefore, the on-board hydrogen production from liquid hydrocarbon sources appears to be a practical option [1,6]. Methanol, ethanol and gasoline have been discussed as candidates; methanol is preferred. Beyond the issues of the storage and transport medium of hydrogen, methanol has a low boiling point, a high hydrogen/carbon ratio and no C–C bonds, and can therefore be reformed at a relatively low temperature, reducing the risk of coke formation during the reaction [3,4].

Methanol can be converted to hydrogen by the following three reactions:



The decomposition of methanol (Eq. (1)) is an endothermic reaction that produces a high yield of CO, which must be transformed into H₂ and CO₂ by the water–gas shift reaction, which is unsuitable for on-board fuel cell applications. The partial oxidation of methanol (Eq. (2)) is an exothermic reaction with a rapid start-up [2], but the formation of hot spots may result in the sintering of the catalysts [5,7]. The steam reforming of methanol (SRM) (Eq. (3)) is also an endothermic reaction and produces the highest yield of hydrogen, about 75%, while maintaining a low selectivity of CO of less than 1% [1,2,5].

Most studies reported in the literature for the SRM reaction were on the application of CuO/ZnO-based and CuO/ZnO/Al₂O₃-based catalysts [1,4,6,8–10]. Alumina is generally added to the catalysts to improve their surface area and mechanical strength, and to prevent catalyst sintering [11,12]. The in situ characterization of CuO/ZnO reveals that the interaction of Cu and ZnO has a pronounced effect on the catalytic activity [9,13]. Zinc oxide is known to improve the dispersion of Cu and the reducibility of CuO. The improvement of reducibility has been proposed as a possible cause of the good activity of CuO/ZnO-based catalysts [3,14]. However, some researchers have proposed that the main reason is the improvement in the adsorption properties, including the adsorption of methanol [15] and the spillover of both hydrogen from Cu to ZnO [16] and oxygen species from ZnO to Cu [17].

To improve the efficiency of catalysts of the SRM reaction, several researchers have introduced a third metallic oxide, ZrO₂, into CuO/ZnO/Al₂O₃ catalysts [3,18–21]. The promoting effect of ZrO₂ has been attributed to the improvement in reducibility [3,18–20]. Agrell et al. [3] used the reduction–oxidation cycle to confirm the enhanced

* Corresponding author. Tel.: +886 3 4227151; fax: +886 3 4252296.
E-mail address: ynzuchen@cc.ncu.edu.tw (Y.-Z. Chen).

reducibility of Zr-containing catalysts. ZrO_2 also reportedly increases the Cu dispersion and prevents the sintering of Cu [18,19], due to its amorphous phase in catalyst. Patel and Pant [21] proposed that ZrO_2 increases the amount of Cu^+ , improving the activity and stability of the catalysts. Likewise, CeO_2 has also been applied to increase the Cu dispersion and the thermal stability of the catalysts [22,23], and even to reduce the CO concentration [23].

The effects of CeO_2 and ZrO_2 have been studied and their roles were proposed, but the compositions of the catalysts for the SRM reaction in related studies are not in the practical range for industrial use [18–25]. The amount of Al_2O_3 used in these studies was always too large to reveal the real effects of CeO_2 [24,25] and ZrO_2 [21], because excess Al_2O_3 inhibits the SRM reaction in CuO/ZnO-based catalysts [3,18]. The aim of this work is to determine the optimal composition of CuO/ZnO/ CeO_2 / ZrO_2 / Al_2O_3 for practical application in the SRM reaction. The commercial catalyst G66B was used as a reference for comparison. The composition (CuO/ZnO/ Al_2O_3 = 30/60/10) of G66B was the starting reference for preparing the CuO/ZnO/ Al_2O_3 -based catalysts. These catalysts with various compositions and containing CeO_2 or ZrO_2 were prepared by co-precipitation. The compositions of the catalysts were systematically changed and the SRM reaction over these catalysts was examined. The synergistic effects among CuO, ZnO, CeO_2 , ZrO_2 and Al_2O_3 were clarified based on N_2O adsorption, temperature-programmed reduction (TPR), X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS) analyses.

2. Experimental

2.1. Preparation of catalysts

CuO/ZnO/ Al_2O_3 -based catalysts that contain CeO_2 or ZrO_2 were prepared by the co-precipitation of a 0.1 M solution of a metal nitrate ($Cu(NO_3)_2$, $Zn(NO_3)_2$, $Al(NO_3)_3$, $Ce(NO_3)_3$, or $ZrO(NO_3)_2$) with a 0.1 M solution of Na_2CO_3 . These two solutions were slowly and simultaneously added to 150 ml of deionized water that was kept at 80 °C with vigorous stirring, while the pH was maintained at 7.0–7.5. The mixture was aged at 80 °C for 2 h with stirring. The precipitate was thoroughly washed with warm deionized water. After being dried at 110 °C for 12 h, the precipitate was calcined at 350 °C for 4 h. The commercial catalyst G66B (Nissan-Girdler) with a weight ratio of 30/60/10 (CuO/ZnO/ Al_2O_3) was used as a starting reference for preparing the CuO/ZnO/ CeO_2 / ZrO_2 / Al_2O_3 catalysts.

2.2. Characterization of catalysts

The chemical compositions of the catalysts were determined by inductively coupled plasma atomic emission spectroscopy, using a JOBIN YVON TY24 instrument. The sample was first dissolved in acidic solutions (mixtures of HNO_3 and HCl , as appropriate), microwaved for 20 min, and then diluted to concentrations within the detection range of the instrument.

X-ray diffraction patterns were collected using a Siemens D8 diffractometer with monochromatic $Cu K_{\alpha}$ radiation ($\lambda = 0.1542$ nm) operated at 40 kV and 40 mA, scanning 2θ from 10 to 90°.

Temperature-programmed reduction was used to characterize the reducibility of the catalyst. TPR experiments were performed in a U-shaped quartz tube that was attached to a thermal-conductivity detector. The sample was pretreated at 200 °C for 1 h in a stream of argon, and then was cooled to room temperature. It was then reduced by increasing the temperature to 350 °C at a rate of 5 °C min^{-1} in a stream of 10% H_2/Ar (30 ml min^{-1}). The water thus produced was trapped using a 3A molecular sieve; hydrogen consumption was monitored using a TCD.

The specific Cu^0 surface areas of the catalysts were determined by the chemisorption of nitrous oxide (10% N_2O/Ar) at 60 °C via

decomposition: $N_2O_{(g)} + 2Cu_{(s)} \rightarrow N_{2(g)} + Cu_2O_{(s)}$. The sample was pre-reduced at 250 °C before chemisorption. The nitrous oxide molecule was assumed to react selectively with the reduced surface copper atom with an $O/Cu_{(s)}$ stoichiometry of 0.5, without the oxidation of the bulk copper. The amount of chemisorbed oxygen ($Cu_2O_{(s)}$) was determined by temperature-programmed reduction, and the Cu surface area was estimated from the surface density of 1.46×10^{19} copper atoms m^{-2} .

X-ray photoelectron spectra were recorded with a PerkinElmer PHI 5000C photoelectron spectrometer at 14 kV and 250 W using $Mg K_{\alpha}$ radiation. The powder samples were pressed into a 10 mm \times 10 mm disk and then fixed on a sample holder placed in a pretreatment chamber. In the chamber, each sample was degassed under 1×10^{-6} Torr for 4 h to remove the volatile contaminants and then was transferred to the analyzing chamber for XPS analysis. All the binding energy (BE) values were calibrated using the C 1s peak at 284.6 eV as a reference.

2.3. Steam reforming of methanol

The SRM reaction was carried out in a fixed bed stainless-steel tubular reactor (18 mm i.d.) that was immersed in a three-sectional temperature-controlled furnace. The SRM reaction was conducted over a temperature range of 200–300 °C at an atmospheric pressure with a catalyst loading of 220 mg in the reactor. The catalyst was pre-reduced in a stream of 10% H_2/N_2 , heated from room temperature to 300 °C and kept at 300 °C for 2 h. The methanol/water (1/1.1 molar ratio) mixture was fed at a constant rate (3.5 ml h^{-1}) using a liquid syringe pump into the upper zone of the reactor that was packed with quartz chips and maintained at the reaction temperature for heating and vaporization. It was then mixed with He (30 ml min^{-1}) as an inert carrier. The exit stream from the reactor was condensed; the gas stream was analyzed online by GC-TCD with a column of 1/8 in. \times 15 ft Carboxen-1000 (60/80), and the condensate was analyzed by GC-FID with a column of 1/8 in. \times 22 ft 15% Carbowax 20 M (80/100).

The conversion of methanol was calculated based on the methanol consumption as $([F]_{in} - [F]_{out})/[F]_{in} \times 100$, where F represents the flow rate of methanol (mol h^{-1}). The selectivity of CO was defined as $[P_{CO}]_{out}/([P_{H_2}]_{out} + [P_{CO_2}]_{out} + [P_{CO}]_{out}) \times 100$, where P is the partial pressure of gaseous products.

3. Results and discussion

The composition of the commercial catalyst G66B (CuO/ZnO/ Al_2O_3 = 30/60/10) was used as a starting reference for preparing the CuO/ZnO/ Al_2O_3 -based catalysts that contained CeO_2 and/or ZrO_2 . The effects of CeO_2/ZrO_2 , ZnO/ ZrO_2 , ZnO/ Al_2O_3 and CuO/ZnO on the SRM reaction were examined and the roles of CeO_2 , ZrO_2 and Al_2O_3 were discussed. The SRM reaction was conducted at the temperatures from 200 up to 300 °C over each catalyst, as shown in Fig. 1. The CuO/ZnO/ Al_2O_3 (30/60/10) that was prepared in this study was more active than the commercial catalyst G66B. The selectivities of H_2 and CO_2 in the outlet gas stream were about 75 and 25% over all of the CuO/ZnO/ Al_2O_3 -based catalysts; such values were rather consistent with the stoichiometry of the SRM reaction. The selectivity of CO was less than 1%.

3.1. Effect of CeO_2/ZrO_2 ratio

Half of the ZnO (30%) in the CuO/ZnO/ Al_2O_3 (30/60/10) catalyst was replaced with CeO_2 and ZrO_2 to yield CuO/ZnO/ $CeO_2/ZrO_2/Al_2O_3$ (30/30/ x/y /10, $x + y = 30$) catalysts, and the effects of CeO_2 and ZrO_2 on the SRM reaction were examined. Table 1 lists the SRM results at 250 and 270 °C over the CuO/ZnO/ $CeO_2/ZrO_2/Al_2O_3$ catalysts. Introducing 30 wt% of ZrO_2 into CuO/ZnO/ Al_2O_3 (30/60/

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