

Short communication

Hydrogen production by steam reforming of methanol in a micro-channel reactor coated with Cu/ZnO/ZrO₂/Al₂O₃ catalyst

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Abstract

Hydrogen production by steam reforming of methanol is studied over Cu/Zn-based catalysts (Cu/ZnO, Cu/ZnO/Al₂O₃, Cu/ZnO/ZrO₂/Al₂O₃). Cu/Zn-based catalysts are derived from hydrotalcite-like precursors prepared by a co-precipitation method. The catalysts are characterized by N₂O chemisorption, XRD, and BET surface area measurements. ZrO₂ added to the Cu/Zn-based catalyst enhances copper dispersion on the catalyst surface. Among the catalysts tested, Cu/ZnO/ZrO₂/Al₂O₃ exhibits the highest methanol conversion and the lowest CO concentration in the outlet gas. A micro-channel reactor coated with a Cu/ZnO/ZrO₂/Al₂O₃ catalyst in the presence of an undercoated Al₂O₃ buffer layer exhibits higher methanol conversion and lower CO concentration in the outlet gas than in the absence of an undercoated Al₂O₃ buffer layer. The micro-channel reactor with a undercoated Al₂O₃ buffer layer produces large amounts of hydrogen compared with one without a buffer layer. The undercoated Al₂O₃ buffer layer enhances the adhesion between catalysts and micro-channel walls, which leads to improvement in reactor performance.

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1. Introduction

Methanol is readily available as a hydrogen source and can be converted into hydrogen-rich gas at moderate temperatures. If methanol is produced from renewable sources, its reforming does not cause a net increase of carbon dioxide in the atmosphere [1]. Thus, steam reforming of methanol has been extensively studied to produce hydrogen for proton-exchange membrane fuel cells (PEMFCs) [2–6]. A typical catalyst systems employed in the steam reforming of methanol include Cu-based catalyst impregnated on γ -Al₂O₃ [7], Cu-based monolith [8], Cu/ZnO catalyst promoted by ZrO₂ and Al₂O₃ [9], Zr-containing CuO/ZnO catalyst [10], and Cu/ZnO/ZrO₂/Al₂O₃ catalyst [11]. It is known that steam reforming of methanol yields a product gas containing up to 75% hydrogen [12]. Equilibrium

conversion in the steam reforming of methanol reaches around 100% at 150 °C and atmospheric pressure [13]. Therefore, steam reforming of methanol has been recognized as a promising route to produce hydrogen for PEMFCs. Nevertheless, the process must meet several requirements, among which one of the most important is that the product gas stream should contain extremely low level of carbon monoxide (a catalyst poison). For the efficient production of hydrogen from methanol, an autothermal micro-channel reactor has been designed and its performance reported [14].

In this work, hydrogen production by steam reforming of methanol is examined over a series of Cu/Zn-based catalysts (Cu/ZnO, Cu/ZnO/Al₂O₃, Cu/ZnO/ZrO₂/Al₂O₃) in a continuous flow fixed-bed reactor. After the catalyst screen test, micro-channel reactors coated with Cu/ZnO/ZrO₂/Al₂O₃ catalyst in the presence/absence of a Al₂O₃ buffer layer are designed, and the effect of undercoated Al₂O₃ buffer layer on reactor performance is evaluated.

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2. Experimental

A series of Cu/Zn-based catalysts (Cu/ZnO, Cu/ZnO/Al₂O₃, Cu/ZnO/ZrO₂/Al₂O₃) were derived from hydrotalcite-like precursors prepared by co-precipitation of metal nitrates in an aqueous solution. Metal nitrates with the desired mole ratios were dissolved in distilled water. The total metal concentration in the aqueous solution was 1 M. A 0.3 M Na₂CO₃ aqueous solution was then added with vigorous stirring under a stream of nitrogen at 60 °C (pH ≈ 9). The precipitates were aged for 3 h and then recovered by filtration, followed by washing with distilled water. The solid product was dried at 100 °C for 12 h, and then calcined at 350 °C for 12 h with an air stream to yield the final form. Prior to the catalytic reaction, each catalyst was reduced in a mixed stream of H₂ (10%) and N₂ (90%) at 350 °C for 3 h.

The catalysts were characterized by X-ray diffraction (Rigaku, D/MAX-2000) and BET surface area analysis (Micromeritics, ASAP 2010). The specific surface area of Cu⁰ in each catalyst was measured by N₂O chemisorption by means of the method described elsewhere [15]. Temperature programmed reduction (TPR) measurements were performed to investigate copper dispersion and reducibility.

A micro-channel reactor, which had a micro-channel sheet with four holes for the flow path and 34 parallel channels of rectangular shape, was used in this work. The dimensions of the micro-channels were 300 μm in width, 200 μm in depth, and 20 mm in length. Two types of micro-channel sheets coated with Cu/ZnO/ZrO₂/Al₂O₃ catalyst were designed, namely, (i) the micro-channel walls were directly coated with Cu/ZnO/ZrO₂/Al₂O₃ catalyst, (ii) Al₂O₃ was introduced as a buffer layer between the Cu/ZnO/ZrO₂/Al₂O₃ catalyst and the micro-channel wall to improve the adhesion between the two components. Coating of the Al₂O₃ buffer was undertaken by the atomic layer deposition (ALD) method. The thickness of the undercoated Al₂O₃ buffer layer was about 0.1 μm.

3. Results and discussion

The physicochemical properties of the prepared catalysts are summarized in Table 1. The Cu/ZnO catalyst showed the lowest BET surface-area (47.5 m² g⁻¹). On addition of the Al₂O₃ and ZrO₂ structural promoters, the surface area increases up to 90.8 m² g⁻¹ for Cu/ZnO/Al₂O₃ and 129.7 m² g⁻¹ for Cu/ZnO/ZrO₂/Al₂O₃. The Cu⁰ surface area determined from N₂O chemisorption monotonically increases on addition of Al₂O₃ and ZrO₂. The Cu/ZnO/ZrO₂/Al₂O₃ catalyst exhibits the highest Cu⁰ surface area. This indicates that the addition of

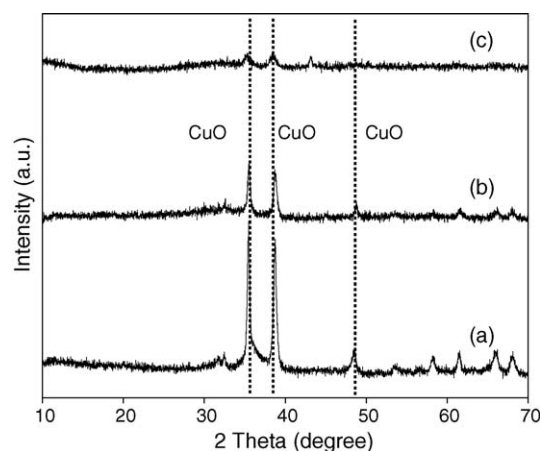


Fig. 1. XRD patterns of (a) Cu/ZnO, (b) Cu/ZnO/Al₂O₃, and (c) Cu/ZnO/ZrO₂/Al₂O₃.

structural promoters such as ZrO₂ and Al₂O₃ provides a large catalyst surface on which copper can be dispersed. Combination of the two metal oxides rather than an individual metal oxide is more efficient. This result is consistent with the findings of Velu et al. [16,17], who demonstrated that substitution of aluminum with zirconium improved copper dispersion and also reducibility.

The XRD patterns of the calcined catalysts are shown in Fig. 1. Peaks indicative of aluminum, zinc, and zirconium phases are not detected, which implies that aluminum, zinc, and zirconium phases are in an amorphous-like or a micro-crystallite state. Only CuO phases appear in a crystal form. The peak intensities of CuO in the Cu/ZnO/ZrO₂/Al₂O₃ catalyst are much weaker than those in the Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts. This indicates that ZrO₂ improves copper dispersion in the Cu/ZnO/ZrO₂/Al₂O₃ catalyst and makes the copper crystallites smaller. It is expected that Cu/ZnO/ZrO₂/Al₂O₃ catalyst with a highly dispersed Cu species may show an excellent catalytic performance in the reaction.

The TPR profiles of the freshly calcined and reoxidized catalysts are shown in Fig. 2. The profile for the Cu/ZnO catalyst shows at least three overlapping peaks. The first reduction starts at 135 °C, and H₂ consumption is maximum at 190 °C. There is also a shoulder peak at about 200 °C, and reduction is completed at around 250 °C. Reoxidation and subsequent reduction of Cu/ZnO increases the particle size, as indicated by the fact that the temperature required for complete reduction increased up to about 290 °C. The freshly calcined Cu/ZnO/Al₂O₃ catalyst is completely reduced at a higher temperature than the Cu/ZnO catalyst. The main peak appears at 240 °C with a long

Table 1
Physicochemical properties of catalysts

Catalyst	Composition (mole%)				BET surface area (m ² g ⁻¹)	Cu ⁰ area (m ² g ⁻¹)
	Cu	Zn	Zr	Al		
Cu/ZnO	50	50	–	–	47.5	20.8
Cu/ZnO/Al ₂ O ₃	50	25	–	25	90.8	23.7
Cu/ZnO/ZrO ₂ /Al ₂ O ₃	50	25	18.75	6.25	129.7	25.9

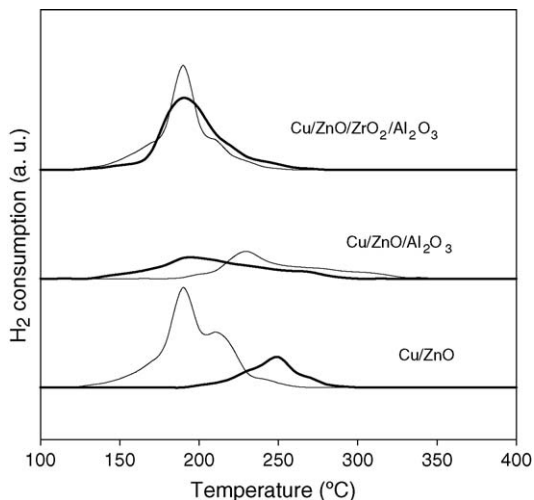


Fig. 2. TPR profiles of freshly calcined (thin line) and reoxidized (thick line) catalysts.

tail extending to 350 °C, which suggests the existence of large CuO crystallites or a strong interaction between copper and support. A strong interaction between copper and the support can also be confirmed from the fact that the XRD peak intensities associated with CuO are relatively weak in the Cu/ZnO/Al₂O₃ catalyst. After reoxidation, the TPR peak of the Cu/ZnO/Al₂O₃

catalyst unexpectedly shifts towards a lower temperature. This indicates that the interaction between copper and support in the Cu/ZnO/Al₂O₃ catalyst decreases after reoxidation. On the other hand, the Cu/ZnO/ZrO₂/Al₂O₃ catalyst exhibits the lowest reduction temperature (190 °C) before and after reoxidation, which indicates the formation of small CuO particles. This, in turn, leads to a high dispersion of Cu species on the catalyst surface. This result is consistent with the Cu⁰ surface area in Table 1, where the highest dispersion of Cu species is observed in the Cu/ZnO/ZrO₂/Al₂O₃ catalyst. Both the reduction profiles of Cu/ZnO/ZrO₂/Al₂O₃ catalyst obtained before and after reoxidation are narrow and almost symmetrical, which suggest a narrow particle size distribution and a homogeneous material composition.

Catalyst screen tests were carried out in a fixed-bed quartz reactor to find the optimum reaction conditions by measuring methanol conversion and CO level in the product gas. The reaction experiments were conducted at temperature of a 180–270 °C with a H₂O:CH₃OH feed mole ratio of 0.6–1.5 for 50 mg of catalyst sample. The total feed flow rate diluted with a helium carrier was 50 ml/min. From a series of catalytic reactions performed with variation of reaction temperature and H₂O:CH₃OH mole ratio, a reaction temperature of 260 °C and a H₂O:CH₃OH mole ratio of 1:3 are found to be the optimum reaction conditions (although the catalytic reaction data are not shown here). The

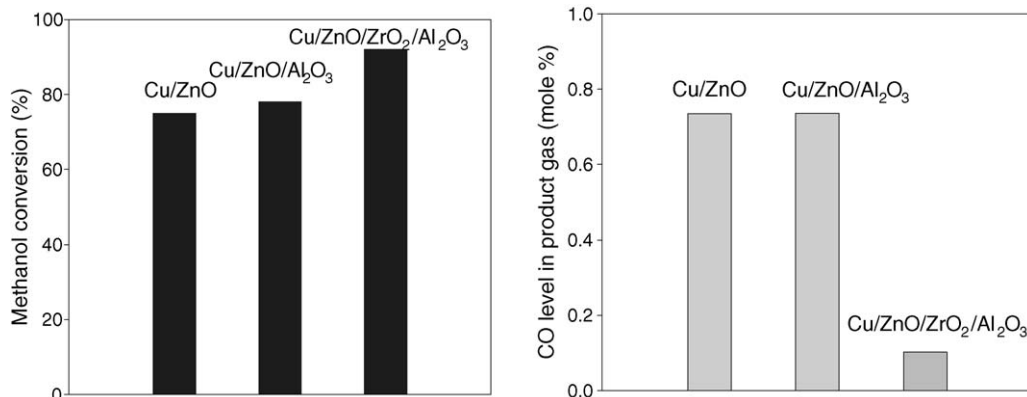


Fig. 3. Methanol conversion and CO level in product gas from steam reforming of methanol at 260 °C and a H₂O:CH₃OH mole ratio of 1:3.

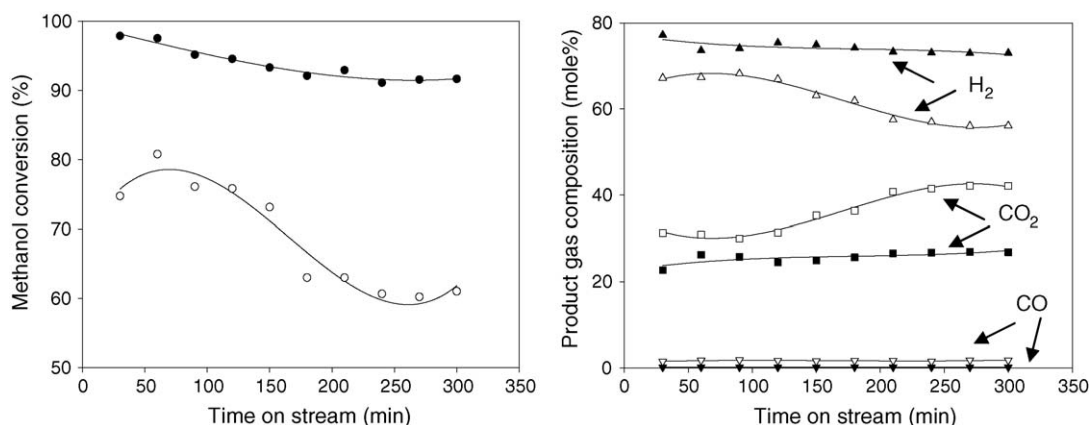


Fig. 4. Performance of micro-channel reactor coated with Cu/ZnO/ZrO₂/Al₂O₃ catalyst for steam reforming of methanol at 260 °C and a H₂O:CH₃OH mole ratio of 1:3 (open symbol, without buffer layer; closed symbol, with buffer layer).

typical catalytic performance obtained at these optimum reaction conditions is given in Fig. 3. The Cu/ZnO/ZrO₂ catalyst shows a slightly enhanced catalytic performance compared with the Cu/ZnO catalyst. On the other hand, the Cu/ZnO/ZrO₂/Al₂O₃ catalyst exhibits the highest methanol conversion and the lowest CO concentration in the outlet gas. The catalyst containing ZrO₂ is highly efficient in the steam reforming of methanol. This may be due to high dispersion of small sized Cu species caused by the addition of a ZrO₂ promoter.

The effect of an undercoated Al₂O₃ buffer layer on the performance of the micro-channel reactor coated with Cu/ZnO/ZrO₂/Al₂O₃ catalyst in the steam reforming of methanol performed at 260 °C and H₂O:CH₃OH mole ratio of 1:3 is shown in Fig. 4. The micro-channel reactor with an undercoated Al₂O₃ buffer layer shows a higher methanol conversion and a lower CO concentration in the outlet gas. The methanol conversion is over 90% and the CO concentration in the outlet gas is less than 0.1%. Furthermore, the micro-channel reactor with an undercoated Al₂O₃ buffer layer produces large amounts of hydrogen compared with the one without buffer layer. It is believed that the undercoated Al₂O₃ buffer layer enhances the adhesion between catalysts and micro-channel walls, and thus, it improves the reactor performance.

4. Conclusions

Hydrogen production by steam reforming of methanol was examined over a series of Cu/Zn-based catalysts. N₂O chemisorption, TPR, and XRD results show that ZrO₂ added to Cu/Zn-based catalysts plays an important role in enhancing copper dispersion and in forming small sized copper particles on the catalyst surface. Among the catalysts tested, the Cu/ZnO/ZrO₂/Al₂O₃ catalyst exhibits the highest methanol con-

version and the lowest CO concentration in the outlet gas. A micro-channel reactor coated with Cu/ZnO/ZrO₂/Al₂O₃ catalyst in the presence of undercoated Al₂O₃ buffer layer gives higher methanol conversion and lower CO concentration in the outlet gas than that in the absence of an undercoated buffer layer. The former produces larger amounts of hydrogen. It is concluded that the undercoated Al₂O₃ buffer layer enhances the adhesion between catalysts and micro-channel walls, and thus improves reactor performance.

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