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Hydrogen production for fuel cells via steam reforming of dimethyl ether over commercial $Cu/ZnO/Al_2O_3$ and zeolite

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ABSTRACT

The steam reforming of dimethyl ether (DME) over physical mixture of commercial $Cu/ZnO/Al_2O_3$ and zeolite (HZSM-5 or HUSY) was extensively studied for the hydrogen production for low-temperature fuel cells. Results indicate that time-on-stream DME conversion, hydrogen yield, and selectivity of carbon-containing products were strongly dependent on the zeolites type and mixing method of the hybrid catalyst. Significantly, the powdery mixture of HUSY and $Cu/ZnO/Al_2O_3$ showed much higher and more stable DME conversion and hydrogen yield than the granular mixture with the same composition. However, when substituting HUSY with HZSM-5 ($SiO_2/Al_2O_3 = 38$), almost the same results were obtained irrespective of the mixing methods. These quite different results were explained based mainly on the acidic properties of the zeolites in combination with the two-step reaction mechanism of the titled reaction. The effect of the types of $Cu/ZnO/Al_2O_3$ and zeolites, weight ratio of $Cu/ZnO/Al_2O_3$ to zeolite, and space velocity on the catalytic performance was quantitatively evaluated. Under optimized conditions, over 80% hydrogen yield was achieved at 100% DME conversion, indicating that commercial catalysts are able to give satisfied results. A scheme for hydrogen production for by burning some unconverted DME outside of the reactor to maintain reaction temperature was proposed and the heat balancing indicated that the steam reforming of DME is very promising to supply hydrogen for fuel cells.

1. Introduction

Due to its low operating temperature, high efficiency, environmental benignity, and high reliability, the proton exchange membrane fuel cell (PEMFC) is perceived as an ideal power for vehicles [1]. Indeed, the technology of PEMFC for electric vehicles has made significant progresses in recent years. However, the supply of the fuel, usually hydrogen, for PEMFC is still a big problem although much work has been done [2]. Among the available choices, hydrogen production via the on-board reforming of hydrogen-rich compounds is believed a reasonable and practical route, and the reforming of various fuels have been reviewed recently [3]. It is clear that the reformate quality via steam reforming is much higher than that via partial oxidation. In comparison with hydrocarbons such as methane, light paraffins, and gasoline, methanol is a more attractive hydrogen-rich compound in the aspect of high hydrogen content, high storage density, and lower reforming temperatures (<623 K). Thus, the steam reforming of methanol (SRM) has received much attention as a promising route for on-board hydrogen production [4].

Remarkably, being an alternative fuel, dimethyl ether (DME) is addressed a cost-effective transition from petroleum to hydrogen in recent years [5]. In comparison with methanol, DME is characterized in, but not limited to, the following merits, e.g., (1) no toxicity or harmlessness (methanol is toxic) [5]; (2) higher hydrogen content (13.0 wt.% vs. 12.5 wt.% of methanol); (3) gas-like property and liquid-storage density [5]; (4) available handling infrastructure (similar to LPG), etc. Furthermore, the steam reforming of DME (SRD) can also proceed at low temperature as well as SRM. Thus, since the publication of the thermodynamics feasible analysis [6] and the pioneering work of Sobyanin and co-workers [7], extensive thermodynamics analyses [8–10] and a few experimental studies have been done on the SRD over Cu-based oxides mixed with alumina [11–24], zeolites [20–28], or solid super acids [29–31], respectively. Moreover, alternative catalysts such as $Ga_2O_3—Al_2O_3$ [32–34], Mo_2C/Al_2O_3 [35], $Cu—Zn/CeO_2—ZrO_2$ catalytic monoliths [36], and noble metals supported on oxides [37–39] are also

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investigated. A comparative and detailed examination of the published works indicate that the principal idea for designing catalyst or interpreting the experimental data is based on the two-step mechanism of the SRD proposed by Sobyanin and co-workers [7] shown as follows.

$$CH_3OCH_3 + H_2O = 2CH_3OH \quad \Delta H^\circ = 37\,\mathrm{kJ\,mol^{-1}}\ \text{(DME hydrolysis)} \tag{1}$$

$$CH_3OH + H_2O = CO_2 + 3H_2 \quad \Delta H^\circ = 49\,\mathrm{kJ\,mol^{-1}}\ \text{(SRM)} \tag{2}$$

$$CH_3OCH_3 + 3H_2O = 2CO_2 + 6H_2 \quad \Delta H^\circ = 135\,\mathrm{kJ\,mol^{-1}}\ \text{(SRD)} \tag{3}$$

It is clear that the SRD (Eq. (3)) is composed of two-consecutive reactions, i.e., DME hydrolysis (Eq. (1)) and the steam reforming of the methanol produced in the first step (Eq. (2)). Therefore, bifunctional catalyst for the SRD is required irrespective of the catalyst systems. Moreover, depending on the catalyst system and reaction parameters, the following side reactions may also occur to different extents.

$$CO_2 + H_2 = CO + H_2O\ \text{(reverse water-gas shift reaction (RWGS))} \tag{4}$$

$$CO + 3H_2 = CH_4 + H_2O\ \text{(methanation reaction)} \tag{5}$$

$$CH_3OCH_3 \rightarrow CH_4 + CO + H_2\ \text{(DME decomposition)} \tag{6}$$

$$2CO{=}C + CO_2\ \text{(Boudouard reaction)} \tag{7}$$

$$CH_3OCH_3 \xrightarrow{\text{Zeolite}} \text{hydrocarbons} \tag{8}$$

$$CH_3OH \xrightarrow{\text{Zeolite}} \text{hydrocarbons} \tag{9}$$

Although the DME hydrolysis is thermodynamically limited, the removal of the produced methanol makes the SRD more favorable at lower temperatures of 423–723 K. Thus, to achieve an optimal hydrogen yield, it is kinetically critical that the rates for the two steps must be sufficiently high and well matched. Unfortunately, the reaction rate of the DME hydrolysis is reported to be slower than that of the SRM [25]. Further experimental results by monitoring the effluent content of methanol suggest that the rate-determine step during the SRD is dependent on the specific catalyst used [20]. Thus, the series-reaction nature of the SRD implies the important role of the synergetic effects between the acidic and reforming catalysts.

Generally, the catalysts investigated are concentrated on alumina or zeolite combined with Cu-based oxides. And the catalytic performance is usually influenced by the hybrid methods of catalysts. When physical mixed, both DME conversion and production rate of hydrogen are found strongly dependent on the mixing method of $Cu/ZnO/Al_2O_3$ and ZSM-5 by Takehira and co-workers [25]. Additionally, the physical mixture of the $Cu/ZnO/Al_2O_3$ and zeolite is more efficient than the co-ion exchanged or impregnated Cu/ZnO/zeolite catalyst for the SRD [21]. Then the cooperation of the catalytic functions in the bifunctional catalyst, i.e., the synergetic effect, must be influenced by the contact states of the catalytic sites. However, the correlation between the contact states of the catalytic active sites over bifunctional catalysts is still not clarified and systematically investigated.

On the other hand, the published works on the SRD are mainly concentrated on the preparation and modification of Cu-based catalysts [11–22,26,27]. In deed, the commercially available $Cu/ZnO/Al_2O_3$, widely used in methanol synthesis, is also active for the steam reforming of methanol and can be used in the SRD. However, the suitability of commercial $Cu/ZnO/Al_2O_3$ for the titled reaction has not been reported.

In this work, hybrid catalyst of various commercial $Cu/ZnO/Al_2O_3$ and zeolites was evaluated. The effect of contact states of $Cu/ZnO/Al_2O_3$ and zeolites, the acidity of zeolites, source of $Cu/ZnO/Al_2O_3$ and operating parameters on the catalytic performance was discussed. A scheme of hydrogen production for PEMFC from SRD was proposed to demonstrate whether the SRD is promising to produce hydrogen for PEMFC even over commercially available catalysts.

2. Materials and methods

2.1. Materials

The hybrid catalyst for the SRD was composed of zeolite and $Cu/ZnO/Al_2O_3$. The commercial products of HUSY (Nankai University Catalyst Co. Ltd.) and HZSM-5 (Nankai University Catalyst Co. Ltd., SiO_2/Al_2O_3 molar ratios of 25, 38, and 50, denoted as ZSM(25), ZSM(38), and ZSM(50), respectively) were calcinated at 500 °C for 3 h to remove any possible volatiles and used as acidic component for the SRD. The commercial $Cu/ZnO/Al_2O_3$ catalysts, which are kindly supplied by the Oxford Catalyst Group PLC (S-28 and S-30), the Northwest Research Institute of Chemical Industry (LC308), and the Changshu Kaituo Catalyst Co. Ltd. (C207-G and C207-Z), were used as received for reforming reaction.

2.2. Preparation of hybrid catalysts

There are two kinds of hybrid catalyst adopted in this work. One is prepared by physical mixture of the 40–60 mesh particles of $Cu/ZnO/Al_2O_3$ and zeolite, named as granular hybrid catalyst (GH). The other is named as powdery hybrid catalyst (PH) prepared as following. The desired amount of zeolite and $Cu/ZnO/Al_2O_3$ were grinded into fine powders, and mixed for 0.5 h in ethanol under ultrasonic conditions (100 W, 40 KHz) to make them mixed uniformly. After evaporation of the ethanol, and the solid powders were dried at 80 °C for 2 h and then pressured, crushed, and sieved into 40–60 mesh particles for reaction test. The weight ratio of to zeolite in the hybrid catalysts was kept at 1/1 if not specified.

2.3. Steam reforming of DME

The SRD reaction was performed in a quartz tube reactor (i.d. 8.0 mm) with hybrid catalyst (0.9 g) at ambient pressure. Priori to reaction, the catalyst was reduced in a diluted H_2 (10 vol.% H_2/N_2) with a temperature programmed procedure to active $Cu/ZnO/Al_2O_3$ catalyst, according to its activation in methanol synthesis, as following: 3 °C $\mathrm{min^{-1}}$ to 110 °C and holding for 0.5 h, 2 °C $\mathrm{min^{-1}}$ to 235 °C and holding for 1 h, 1 °C $\mathrm{min^{-1}}$ to 260 °C and holding for 0.5 h, 1 °C $\mathrm{min^{-1}}$ to 285 °C and holding for 0.5 h. When the reaction temperature was adjusted to 290 °C, the SRD reaction was initiated with a gas mixing of 10% DME, 40% of H_2O and N_2 (balance) ($DME/H_2O/N_2 = 1/4/5$ (molar ratio)) at GHSV of 4000 $\mathrm{h^{-1}}$. The deionized water was injected with an HPLC syringe pump and evaporated at 150 °C.

2.4. Product analysis

The products were analyzed with an online gas chromatography (GC-9560, Huaai Chromatographic Analysis Co. Ltd.) equipped with pneumatically controlled 10-port and 4-port valves and serially connected thermal conductivity detector (TCD) and flame ionization detector (FID). To prevent the condensation of any products, the lines and valves between the outlet of the reactor and the inlet of the GC column were kept at above 150 °C. Three packed columns were applied to separate the products. A Porapak R column was used as a pre-separation column to separate the analytes into two groups. One group containing H_2, N_2, CO, and CH_4 was separated with a 13× zeolite column. The C_3–C_4 hydrocarbons, DME, H_2O,