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Generating hydrogen-rich fuel-cell feeds from dimethyl ether (DME) using Cu/Zn supported on various solid-acid substrates

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Abstract

Several incipient wetness prepared catalysts containing copper and zinc were prepared in-house and reactor tested for the production of hydrogen from dimethyl ether steam reforming (DME-SR). The incorporation of copper and zinc onto a solid acid substrate (viz., zeolites ZSM-5 and Y with Si/Al = 2.5–140, γ-Al_2O_3, and ZrO_2) combined the catalytic components for DME hydrolysis to methanol (MeOH) and methanol steam reforming (MeOH-SR) into a single catalyst. Catalyst characterizations included BET surface areas, metal loading, acidity measurements using isopropyl amine, thermogravimetric uptakes of DME, and X-ray diffraction studies. One co-ion exchange sample was tested and was found to be inactive toward DME-SR because of its inactivity toward methanol steam reforming. The most active catalyst was copper–zinc supported on γ-Al_2O_3, reaching an equilibrium predicted hydrogen yield of 89% (steam-to-carbon ratio (S/C) = 1.5, space-time(τ) = 1.0 s, $T = 400$ °C, and $P_{abs} = 0.78$ atm). Of the zeolite-supported Cu/Zn catalysts, copper–zinc supported on zeolite ZSM-5 with a Si–Al ratio of 25 was observed to be the most active with a hydrogen yield of 55% (S/C = 1.5, $\tau = 1.0$ s, $T = 275$ °C, and $P_{abs} = 0.78$ atm).

Keywords: Dimethyl ether; Hydrolysis; Zeolites; Methanol; Alumina; Zirconia; Acidity; ZSM-5; Y; Steam reforming; Hydrogen; Fuel cells

1. Introduction

A promising alternative fuel is dimethyl ether (DME) because of its proposed uses as a diesel substitute (cetane #: 55–60) and as a source of hydrogen-rich fuel-cell feeds [1]. DME as a fuel for solid-oxide fuel cells is also being researched [2,3]. A review of the advantages of dimethyl ether over the other candidate fuels (e.g., Fischer–Tropsch fuels, biodiesel, methanol, ethanol, methane, etc.) as an alternative fuel are presented elsewhere [1,4,5].

Currently, dimethyl ether is produced commercially from a two-step process. The first step is methanol synthesis from syngas (typically from natural gas, although coal and biomass are viable sources of syngas); the second step is the dehydration of methanol to dimethyl ether over solid-acid catalysts (e.g., ZrO_2 [6], γ-Al_2O_3 [7–11], zeolites [8,10,12,13], and Cab-O-Sil [14]). Single-step processes for converting syngas directly to DME are being researched [15–27].

Because of the principle of microscopic reversibility, the solid-acid catalysts employed for methanol dehydration to DME can also be employed for the hydrolysis of dimethyl ether to methanol (the reverse of methanol dehydration), but the principle of microscopic reversibility makes no predictions on the absolute rates or the conditions needed for the reaction to proceed. For example, methanol dehydration over γ-Al_2O_3 occurs in the temperature range of 200–300 °C [8,9], while the hydrolysis of DME to methanol over γ-Al_2O_3 occurs in the temperature range of 300–400 °C [28] because of the potential inhibiting effects of adsorbed water on γ-Al_2O_3 [13].

The advantage of methanol dehydration to DME is the large equilibrium conversions of methanol (at 300 °C the equilibrium conversion of MeOH is ~86%) [5,29]; the opposite is true for the reverse reaction where the equilibrium conversion of dimethyl ether is approximately 14% (at S/C = 0.5 and $T = 300$ °C) [29]. Our previous research indicated that the acid-catalyzed hydrolysis of dimethyl ether to methanol reaches equilibrium over ZSM-5 catalysts (Si/Al = 15, 25,

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40) at a temperature of 200 °C (S/C = 1.5, $\tau = 1.0$ s, and $P_{abs} = 0.78$ atm) [5,28]; however, because of the low equilibrium conversions of DME, the question remains whether or not the rates of DME hydrolysis to MeOH are suitable for the production of hydrogen-rich fuel-cell feeds when a methanol steam reforming catalyst is combined with a DME hydrolysis to MeOH solid-acid catalyst.

The acid catalyzed hydrolysis of dimethyl ether to methanol was reported for several acid catalysts (i.e., zeolites Y and ZSM-5, γ-Al_2O_3, and ZrO_2) and non-acid catalysts (Cu/Zn/Al_2O_3 (BASF K3-110, denoted as K3), and SiO_2) [28]. Silica and BASF K3-110 were observed to be ineffective in converting DME to MeOH during dimethyl ether hydrolysis. Zirconia was the only acid catalyst that did not reach methanol mole percentage values predicted by equilibrium [5,29]. Zeolite ZSM-5 having Si–Al ratios of 15, 25, and 40 all attained equilibrium at approximately 200 °C; zeolite ZSM-5 (Si/Al = 140) and zeolites Y (Si/Al = 2.5 and 15) attained equilibrium at a temperature of approximately 250 °C, while γ-Al_2O_3 attained equilibrium at approximately 350 °C [29].

Research efforts on the production of hydrogen from dimethyl ether have been published [5,30–38]. The researchers approach in producing hydrogen from DME was a two-step process—the first step is the acid catalyzed hydrolysis of dimethyl ether to methanol (Eq. (1)), followed by methanol steam reforming (Eq. (2)) over Cu or Cu/ZnO. Dimethyl ether steam reforming (Eq. (3)) is a linear combination of Eq. (1) and Eq. (2).

- DME hydrolysis:

$$(CH_3)_2O + H_2O \rightleftharpoons 2CH_3OH \qquad \Delta H_r^0 = +36.6\,\text{kJ/mol}, \quad \Delta G_r^0 = +15.9\,\text{kJ/mol} \tag{1}$$

- MeOH steam reforming:

$$CH_3OH + H_2O \rightleftharpoons 3H_2 + CO_2 \qquad \Delta H_r^0 = +49.1\,\text{kJ/mol}, \quad \Delta G_r^0 = -0.4\,\text{kJ/mol} \tag{2}$$

- DME steam reforming:

$$(CH_3)_2O + 3H_2O \rightleftharpoons 6H_2 + 2CO_2 \quad \Delta H_r^0 = +135.0\,\text{kJ/mol}, \qquad \Delta G_r^0 = +15.0\,\text{kJ/mol} \tag{3}$$

Two approaches to DME-SR have been employed: (1) physical mixtures of a DME hydrolysis catalyst (i.e., solid-acid catalyst) and a methanol steam reforming catalyst (typically Cu-based), and (2) supported catalysts that combined the DME hydrolysis and MeOH-SR components into a single catalyst. Additional methanol steam reforming catalyst formulations consisted of noble metals (i.e., Pt, Rh, and Ru) as the active catalytic agent or as promoters [34]. The effect of promoters (e.g., Fe, Cr, Ce, Mg, and Mn) were also investigated [35,37].

The major differences in the research efforts were the catalyst preparation methods. It is known that the catalyst preparation method can affect the catalyst activity and catalyst durability. The major similarities between the studies were the catalytic components used for DME hydrolysis and methanol steam reforming. Copper was predominately used as the methanol steam reforming component and alumina was predominately used as the DME hydrolysis component.

Research efforts were undertaken by Takeishi and Suzuki [34], Tanaka et al. [35], and Bhattacharyya and Basu [30] in formulating methanol steam reforming catalysts, but little attention was given to the dimethyl ether hydrolysis component, evidenced by the use of alumina in their catalyst studies. Because the methanol steam reforming components were non-acid catalysts, their research efforts were essentially examining the effects of catalyst preparation and promoters on methanol steam reforming.

The research by Yamada et al. [39], Galvita et al. [31], and Semelsberger et al. [5,38] investigated heteropolyacids (HPA) or zeolites as acid catalysts for DME hydrolysis. The physical mixture of Cu/SiO_2 and HPA/$A1_2O_3$ prepared by Galvita was active toward dimethyl ether steam reforming ($X_{DME} = 100\%$, $\tau = 3.0$ s, CO selectivity = 9.5%, CO_2 selectivity = 90.5%, $T = 290$ °C). Selectivity was defined as the amount of CO (or CO_2) relative to the total amount of carbon containing products (e.g., CH_4, CO, CO_2, etc.).

Our previous research presented the results of DME steam reforming over physical mixtures containing equal amounts (by volume) of a commercial Cu/Zn/Al_2O_3 catalyst (BASF K3-110, denoted as K3) and several solid-acid catalysts (viz., zeolites ZSM-5 (Si/Al = 15, 25, 40, 140), zeolites Y (Si/Al = 2.5 and 15), γ-Al_2O_3, and ZrO_2) [38]. For benchmarking purposes, methanol steam reforming was also performed over K3. Dimethyl ether steam reforming using the physical mixtures of K3 + Z(15), K3 + Z(25), and K3 + Z(40) showed high hydrogen yields ($Y_{H_2} \approx 94\%$, $T = 275$ °C, $\tau = 1.0$ s, S/C = 1.5) and hydrogen selectivities ($S_{H_2} \approx 96\%$, $T = 275$ °C), comparable to those observed for MeOH-SR over K3 ($Y_{H_2} \approx 96\%$, $S_{H_2} \approx 99\%$, $T = 225$ °C, $\tau = 1.0$ s, S/C = 1.0) [38].

With the performances of the physical mixtures established [38], the goal is to combine the DME hydrolysis component (i.e., solid-acid catalyst) with the MeOH-SR component (i.e., copper and zinc oxide) into a single catalyst while maintaining comparable activities or surpassing those observed with physical mixtures. This paper presents the performances of incipient wetness prepared Cu–Zn catalysts supported on various solid-acid catalysts for the production of hydrogen from dimethyl ether. Zeolite ZSM-5 (Si/Al = 15) co-ion exchanged with copper and zinc was also investigated. The objectives of this study were:

- to compare the activities, selectivities, and hydrogen yields of the various in-house prepared catalysts as a function of solid-acid support,
- to compare the performances of the in-house prepared catalysts to those of physical mixtures toward dimethyl ether steam reforming, and
- to compare the activities, selectivities, and hydrogen yields of the various in-house prepared catalysts toward methanol steam reforming.