Direct synthesis of dimethyl ether from syngas over Cu-based catalysts: Enhanced selectivity in the presence of MgO

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ABSTRACT

Direct synthesis of dimethyl ether (DME) from syngas was investigated over a series of hybrid catalytic systems containing a Cu-based methanol synthesis component with varying amounts of ZnO and MgO, and γ-Al_2O_3 as a methanol dehydration component. Methanol synthesis and methanol dehydration components were homogeneously mixed in a 2:1 weight ratio to prepare the hybrid catalysts, which were characterized by transmission electron microscopy, scanning electron microscopy, BET surface area analysis, powder X-ray diffraction, NH_3 temperature-programmed desorption, and H_2 temperature-programmed reduction methods. The syngas-to-DME (STD) reaction was studied in an isothermal fixed bed reactor at 30 bar and 260 °C. The catalysis results revealed improved effectiveness of the catalyst in the presence of 20 mol% MgO, enabling a significant enhancement in CO conversion from 19% to 37% and in DME selectivity from 36% to 83%, as compared with the activity of a catalyst without MgO. By-product CO_2 and C_1 and C_2 hydrocarbon selectivity was also decreased from 48% to 14% for CO_2 and from 8% to 2.5% for hydrocarbons. Catalyst performance, CO conversions and DME selectivity were evaluated by varying the reaction temperature, pressure, space velocity and H_2/CO ratio in syngas. XRD data revealed the formation of a good crystalline malachite structure for the catalysts containing up to 20 mol% MgO, but the crystallinity in the structure was lost when 30% MgO was added, resulting in decreased catalytic activity.
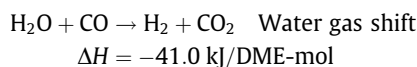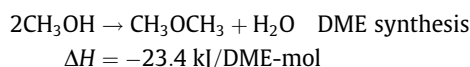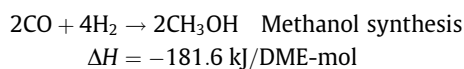
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1. Introduction

Dimethyl ether (DME) is gaining considerable attention worldwide as a cleaner fuel because of its environmentally benign fuel properties [1,2]. DME is a colorless gas (at STP) and can be liquefied at about 6 atm at 25 °C, which allows its usage on the same platform as current Liquefied Petroleum Gas (LPG) storage and distribution technologies with minor modifications [3]. The cetane number of DME (55–60) is higher than that of diesel oil ($\sim$50). DME is also an excellent feedstock and intermediate for methyl acetate, dimethyl sulfate, and light olefins [4].

Conventionally, DME is produced via a two-step process. The first step is the catalytic conversion of syngas to methanol and the second step is the dehydration of methanol over alumina or zeolite-based acidic materials [5]. Methanol synthesis is a high-temperature and high-pressure process and is limited by thermodynamic constraints. Because of the very low equilibrium of the conversion of syngas to methanol, direct conversion of syngas to DME (STD) has inherent thermodynamic advantages in achieving higher syngas conversion, and thus overall economy of the process [6–8]. The key steps in the STD process are as follows:

$$2CO + 4H_2 \rightarrow 2CH_3OH \quad \text{Methanol synthesis}$$
$$\Delta H = -181.6 \text{ kJ/DME-mol}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad \text{DME synthesis}$$
$$\Delta H = -23.4 \text{ kJ/DME-mol}$$

$$H_2O + CO \rightarrow H_2 + CO_2 \quad \text{Water gas shift}$$
$$\Delta H = -41.0 \text{ kJ/DME-mol}$$

Since direct conversion of syngas to DME also involves in situ methanol formation, the catalyst for the STD process must contain bifunctional sites for methanol synthesis and its subsequent dehydration. The most common hybrid catalysts containing bifunctional sites for direct conversion of syngas to DME are prepared either by physical mixing of both components or through co-precipitation of methanol synthesis catalyst and its subsequent impregnation on methanol dehydration catalyst [9–11]. In this process, DME selectivity strongly depends on the catalyst properties, such as acidity, nature of acid sites, pore size, and crystallinity, and the reaction factors, such as temperature, pressure, and space velocity of the feed stream. Under comparable operating conditions, the rate of methanol conversion and the selectivity of DME are governed by the physiochemical properties of the catalytic materials. Side reactions such as Fischer–Tropsch (FT), water gas shift, methanation, and coke formation may cause lower DME selectivity in the STD process. Therefore, the catalyst must have the ability to suppress these side reactions to enhance DME selectivity.

Currently Cu–ZnO–Al$_2$O$_3$ catalyst, containing Cu and Zn in a ratio of 70:30, is used in industrial processes for methanol synthesis [12,13]. It is known from the literature that the presence of Cu in metallic Cu^0 form with a high degree of dispersity is essential to achieve high selectivity for methanol formation [14]. Cu dispersion and its intrinsic activity are beneficially influenced by the homogeneous presence of ZnO in the catalyst. The latter component acts as a geometrical spacer between Cu nanoparticles [15], which helps to disperse Cu in the course of catalyst preparation [12], and hence to achieve a high surface area of Cu. A high surface area of Cu per unit weight of catalyst is necessary to achieve high selectivity in methanol formation. Additionally, strong metal–support interaction (SMSI) between ZnO and Cu is believed to affect the in situ formation of catalytically active sites. Recently, Behrens and co-workers have reported that ZnO promotes SMSI with Cu, which induces the formation of "methanol-active copper." Different models for this synergy have been discussed in the literature [16–20]. The defect sites in the catalysts can also influence methanol formation [16].

Variation of reaction parameters during catalyst preparation may lead to the formation of different hydroxycarbonate precursor phases, the most preferred being zincian malachite ((Cu,Zn)$_2$(OH)$_2$ CO$_3$) [12]. It is well known that incorporation of Zn^{2+} into the crystal lattice of malachite favors aggregation of the CuO/ZnO nanostructure upon calcination due to the favorable distribution of both species in the crystal lattice of the precursor compound [21]. However, incorporation of Zn^{2+} into the malachite crystal lattice is also limited to <30% by chemical constraints [22]. A small amount of Al$_2$O$_3$ acts as a structural promoter in the methanol synthesis catalyst [23,24], though Al^{3+} incorporation into the malachite structure can cause charge mismatch. MgO can be an interesting replacement for Al^{3+} because of the similar charge of Mg^{2+} and Zn^{2+}, and the only 2% smaller ionic radius of Mg^{2+} than of Cu^{2+}. Thus, more Cu dispersion per unit weight of catalyst can be expected in the presence of MgO. Recent studies have shown that MgO has the potential to serve as an effective structural promoter, demonstrating its ability to reduce the reaction temperature, and hence to (i) achieve high selectivity for the desired products by lowering by-products formation, (ii) inhibit premature catalyst sintering, (iii) improve conversion rates of substrates, and (iv) increase the active metal surface area [25,26]. Fitzpatrick et al. have reported that the activity of the Cu–ZnO catalyst for methanol synthesis improves significantly in the presence of MgO [27]. The presence of MgO in the catalyst also reduces by-product formation. Among several promoters tested (SiO$_2$, MnO, Al$_2$O$_3$, MgO), the authors reported that the highest Cu surface area and methanol selectivity were achieved by the catalyst that contained 1.5 wt.% MgO.

Subsequent dehydration of methanol to DME takes place in the presence of an acidic catalyst. Solid acid catalysts, such as HZSM-5, H-beta, SAPO's, γ-Al$_2$O$_3$, TiO$_2$, SiO$_2$–Al$_2$O$_3$, and Al$_2$O$_3$–TiO$_2$, have been used for the dehydration of methanol in the temperature range of 250–400 °C [28–31]. Mao et al. have studied the activity of a bifunctional catalytic system containing MgO-modified HZSM-5 and Cu/ZnO/Al$_2$O$_3$ in direct conversion of syngas to DME [32]. The authors reveal that MgO helps in neutralizing the stronger acid sites to weaker sites. The strong acidic sites are reported to enhance DME degradation to lower hydrocarbons [10].

Although Mao et al. have reported the beneficial effect of MgO in methanol dehydration, the role of MgO in the bifunctional catalyst for the STD process has yet to be investigated. Therefore, it is worthwhile to study the effect of MgO on the properties of the hybrid Cu/ZnO/MgO–γ-Al$_2$O$_3$ catalyst and its catalytic effectiveness for direct conversion of syngas to DME. Additionally, we studied the combined effects of ZnO and MgO on Cu-based hybrid ternary catalytic systems by changing the weight ratio of ZnO and MgO in the catalyst compositions.

Among three different acidic materials (γ-Al$_2$O$_3$, HZSM-5, SiO$_2$–Al$_2$O$_3$) used in the formulation of the hybrid catalysts, γ-Al$_2$O$_3$ was found to be most effective in combination with Cu/ZnO/MgO, which showed constant methanol conversion over a longer reaction time with high selectivity to DME. Thus, γ-Al$_2$O$_3$ was selected as a component for methanol dehydration in the hybrid catalyst. Furthermore, it is known that γ-Al$_2$O$_3$ can resist structural changes during methanol dehydration because of its high hydrothermal stability, and thus minimize the formation of undesired side products [33,34]. The focus of this study is on evaluating the structural and physicochemical properties of the catalysts as a function of MgO content and the effect of these catalytic properties on the conversion of syngas, and DME yield and selectivity.

2. Experimental

2.1. Chemicals

Copper nitrate (Cu(NO$_3$)$_2$·2.5H$_2$O) and zinc nitrate (Zn(NO$_3$)$_2$·XH$_2$O) were purchased from Alfa Aesar. Magnesium nitrate (Mg(NO$_3$)$_2$·6H$_2$O) and sodium carbonate were obtained from Acros India and Merck India, respectively. All chemicals were used as received.

CuO/ZnO/MgO catalyst was prepared by a co-precipitation method. A 1000 mL aqueous solution containing copper nitrate, zinc nitrate, and/or magnesium nitrate salts of total molarity 1.0 M and a 500 mL aqueous solution of Na$_2$CO$_3$ of 0.5 M were mixed in dropwise fashion in a 2 L jacketed reactor containing 500 mL of distilled water. The jacketed reactor (Fig. S1 in the Supporting Information) was stirred continuously at 350 rpm and 70 °C during the mixing of the two solutions. The pH of the mixture was maintained at 7 during precipitation by controlling the flow rates of the two solutions. After complete precipitation, the precipitates were aged for 1 h at 70 °C. The precipitate was then filtered and washed several times with distilled water to remove residual sodium ions. Complete removal of Na$^+$ and other ions was confirmed by the conductivity measurement of the filtrate. The precipitate was washed until the conductivity of the filtrate was similar to that of distilled water. The washed solid was dried at 80 °C in a furnace for 12 h and subsequently calcined under air at 400 °C for 4 h. Other catalysts (Table 1) were prepared following a similar procedure. The atomic percentage of each metal in the catalyst, as listed in Table 1, represents their theoretical values. Hereafter, the catalysts are represented by the presence of metal components in which Cu, Zn, and Mg are abbreviated as C, Z, and M, respectively.