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One-step synthesis of dimethyl ether from the gas mixture containing CO_2 with high space velocity

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ABSTRACT

Dimethyl ether (DME) has been considered as a potential hydrogen carrier used in fuel cells; it can also be consumed as a diesel substitute or chemicals. To develop the technique of DME synthesis, a bifunctional Cu–ZnO–Al_2O_3/ZSM5 catalyst is prepared using a coprecipitation method. The reaction characteristics of DME synthesis from syngas at a high space velocity of 15,000 mL $(g_{cat}\,h)^{-1}$ are investigated and the effects of reaction temperature, pressure, CO_2 concentration and ZSM5 amount on the synthesis are taken into account. The results suggest that an increase in CO_2 concentration in the feed gas substantially decreases the DME formation. The optimum reaction temperature always occurs at 225 °C, regardless of what the pressure is. It is thus recognized that the DME synthesis is governed by two different mechanisms when the reaction temperature varies. At lower reaction temperatures (<225 °C) the reaction is dominated by chemical kinetics, whereas thermodynamic equilibrium is the dominant mechanism as the reaction temperature is higher (>225 °C). For the CO_2 content of 5 vol.% and the pressure of 40 atm, the maximum DME yield is 1.89 g $(g_{cat}\,h)^{-1}$. It is also found that 0.2 g of ZSM5 is sufficient to be blended with 1 g of the catalyst for DME synthesis.

1. Introduction

In recent years, the applications of dimethyl ether (DME) in industries are receiving considerable attention. In chemical industries, DME is a useful intermediate for producing chemicals, such as methyl acetate, dimethyl sulfate and light olefins [1,2]. Meanwhile, DME has been considered as a potential diesel substitute used in compression ignition engines because of its high cetane number (i.e. 55–60) [3,4]. DME also possesses the merit of environmentally friendly properties [5]. A comparison to gasoline combustion, burning DME in diesel engines emits much less air pollutants, such as NO_x, CO, hydrocarbons and particulate matters [6–8]. DME can be efficiently reformed to hydrogen at lower temperatures so that it is also considered as a promising feedstock for fuel cells [9,10]. Although DME is a volatile organic compound (VOC) with the boiling temperature of −25 °C at the atmospheric pressure, it is non-carcinogenic, non-teratogenic, non-mutagenic and non-toxic [11]. This implies that the risk in damaging health from consuming DME is slight.

DME synthesis plays a crucial role in extending its applications. Conventionally, DME is produced through a two-step process or indirect method. In this route, methanol is first synthesized from syngas (i.e. CO + H_2); then, DME is produced from the dehydration of methanol [12–15]. The reactions in the two-step process are expressed as:

Methanol synthesis

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H^0 = -90.6\ \text{kJ/mol} \tag{1}$$

Methanol dehydration

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad \Delta H^0 = -23.4\ \text{kJ/mol} \tag{2}$$

Apart from the two-step process, DME can also be generated from syngas via a one-step process, namely, the direct method. In addition to the methanol synthesis and dehydration, the direct method is also related to water gas shift reaction (WGSR) [13,16–19]. The reaction is given by:

Water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0 = -41.2\ \text{kJ/mol} \tag{3}$$

Accordingly, the net reaction in the direct method is

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \quad \Delta H^0 = -245.8\ \text{kJ/mol} \tag{4}$$

This method for the production of DME has attracted more and more industrial interest because of its lower thermodynamic limitation as well as higher economic value and theoretical significance [17,20].

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When DME is synthesized from syngas through the direct method, the development of bifunctional catalysts is a key factor in determining the performance. As the name implies, two types of active site are simultaneously contained in a bifunctional catalyst, with one for methanol synthesis and the other for methanol dehydration [20,21]. Cu–ZnO–Al_2O_3 catalysts are the most commonly employed catalysts for methanol synthesis in industry. In Cu–ZnO-based catalysts, metallic copper clusters are the active sites for methanol synthesis reaction, and ZnO plays a pivotal role in maintaining the active copper metal in optimal dispersion [22]. In other words, the main function of ZnO is to increase Cu dispersion in the calcined sample, thus providing a high number of active sites exposed to gaseous reactants. The purpose of addition of M^{3+} ions (e.g. Al^{3+}) into Cu–ZnO-based catalysts is to increase their surface areas and copper dispersion; it is also able to inhibit the sintering of Cu particles at on-stream conditions [22,23]. In regard to methanol dehydration, the commonly employed solid acid catalysts include γ-Al_2O_3, silica–alumina and zeolites such as HZSM-5, HY, HMCM-49, HMCM-22, SAPOs and Ferrierite. Among these catalysts, HZSM5 has been extensively employed due to its high catalytic activity for the conversion of syngas to methanol at certain reaction temperatures [24,25]. In the study of An et al. [26], it was reported that more water was produced in the process of CO_2 hydrogenation compared to CO hydrogenation, and ZSM5 was not sensitive to the concentration of water. On the other hand, Yang et al. [27] addressed that the methanol dehydration catalyst (or zeolite catalyst), such as ZSM5, had more activity and stability than γ-Al_2O_3 catalyst. Moreover, Aguayo et al. [28] pointed out that CuO–ZnO–Al_2O_3/NaHZSM5 catalyst had an excellent performance and it was suitable for using it in uninterrupted reaction–regeneration cycles. For these reasons, ZSM5 zeolite was chosen in the present study.

DME synthesis has been reported in some studies; however the information concerning its production process remains insufficient. For instance, when syngas is produced from the gasification of biomass and steam reforming of hydrocarbons and used as the feedstock for DME production, CO_2 is inevitably contained in the feed gas [20,29,30]. However, relatively little research has been performed on the role played by CO_2 upon DME synthesis, especially at the conditions of high space velocity. From Eq. (4), it is known that a higher CO_2 concentration disadvantages DME formation. Nevertheless, if CO_2 is removed prior to carrying out DME synthesis, an extra operating cost for CO_2 separation is required. To provide an in-depth observation on DME synthesis, a bifunctional catalyst for directly producing DME from syngas will be prepared and tested in the present study. Particular attention is paid to the influence of CO_2 on DME formation at a high space velocity. A comparison between the present study and others will be made as well.

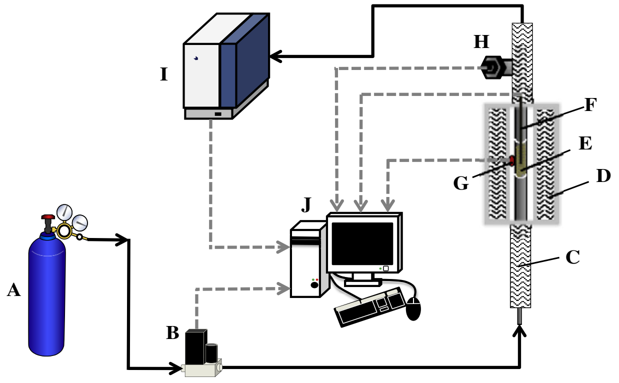

Fig. 1. A schematic of the reaction system (A: feed gas; B: mass flow controller; C: heating tape; D: reactor; E: catalyst bed; F: thermocouple; G thermocouple; H: back pressure valve; I: microgas chromatography; J: recorder).

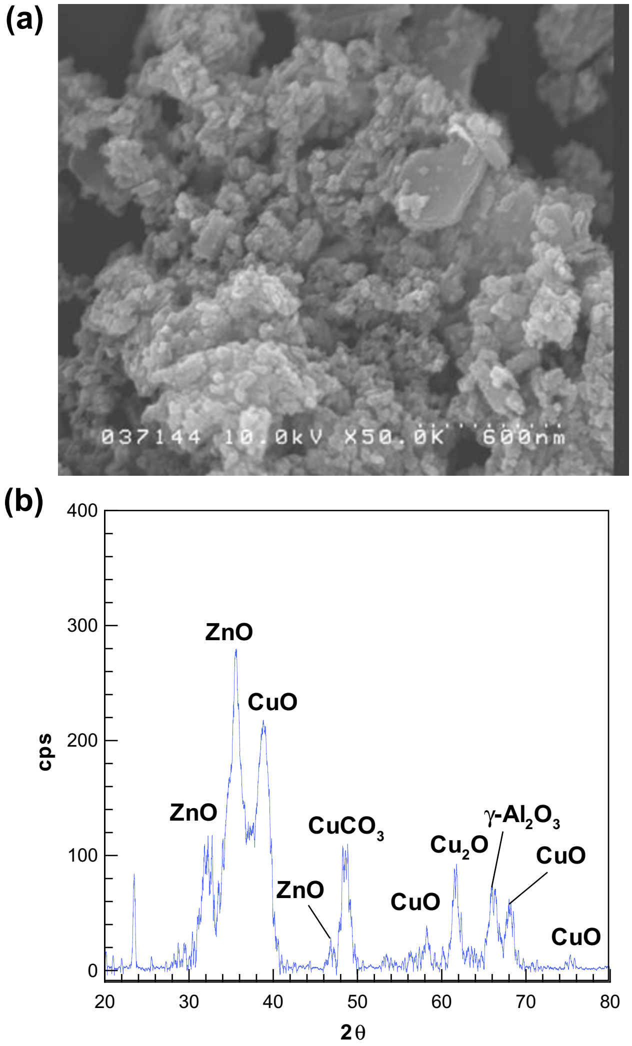

Fig. 2. (a) SEM image (×50,000) and (b) XRD pattern of the fresh prepared CuO–ZnO–Al_2O_3 catalyst.

2. Experimental

2.1. Catalyst preparation

The catalyst used for synthesizing DME was a Cu–ZnO–Al_2O_3 catalyst which was prepared by a coprecipitation method. A solution of $Cu(NO_3)_2{\cdot}2.5H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ and a solution of Na_2CO_3 were individually prepared. Then, a beaker containing deionized water was heated to 70 °C. The two solutions were simultaneously added drop wise to the beaker with the period of 60 min by controlling the flow rates of the two solutions at pH = 7 under continuous stirring so that the coprecipitation was achieved. The suspension was aged for 3 h followed by filtered out, washed and dried at 120 °C for 12 h. Then the precipitate was calcined in air by raising temperature to 350 °C with the heating rate of 1 °C min^{-1} followed by soaking it at 350 °C for 2 h. The prepared Cu–ZnO–Al_2O_3 catalyst was mixed with ZSM5 to form the bifunctional catalyst. In the prepared catalyst, the weight percentages of Cu, Zn and Al were 47.3, 23.9 and 2.9 wt.%, respectively. Accordingly, the atomic ratio between the three metals Cu, Zn and Al was 1:0.490:0.144. The BET surface area, pore volume and