Direct dimethyl ether synthesis from syngas on copper–zeolite hybrid catalysts with a wide range of zeolite particle sizes

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ABSTRACT

This paper reports on direct dimethyl ether synthesis from syngas on hybrid bifunctional copper–zeolite catalysts. Both laboratory synthesized and commercial zeolites were used in this work. The catalyst performance is evaluated under pressure in a continuous fixed bed milli-reactor. The relationships between zeolite particle sizes, acidity and catalytic performance of the hybrid catalysts in dimethyl ether synthesis have been studied. The catalysts and catalyst precursors were characterized using a wide range of characterization techniques: nitrogen adsorption–desorption measurements, X-ray diffraction, ^{27}Al NMR, scanning electron microscopy, transmission electron microscopy and Fourier transform infrared spectroscopy with adsorbed molecular probes.

It is found that the reaction rate in direct dimethyl ether synthesis is strongly affected by the sizes of zeolite particles. The hybrid catalysts containing small individual nanosized zeolite particles (60–100 nm) were much active than their counterparts with intergrown crystal agglomerates. The phenomenon is interpreted in terms of enhanced transport of methanol from the copper catalyst to the acid sites in the small zeolite particles with a shift of the thermodynamic equilibrium. The catalyst deactivation was attributed to copper sintering in the presence of the acid sites on the external surface of zeolites. It is established that the catalyst deactivation is less significant with the catalysts containing ZSM-5 zeolites with lower concentration of acid sites on the zeolite external surface. A new methodology to enhance the catalytic performance and stability of copper–zeolite hybrid catalysts for direct dimethyl ether synthesis is proposed.
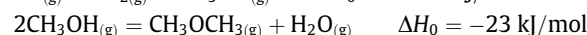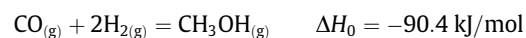
1. Introduction

Dimethyl ether (DME) is the simplest ether and is one of the most promising environmentally optimized alternatives [1,2] to the conventional fossil diesel fuels due to its high cetane index (>55), low emission of CO, NO_x, particulates and reduced noise. DME can be used as a substitute for liquefied petroleum gas (LPG) that is widely used as fuel in the industry and household [3].

DME has several interesting characteristics as a fuel. It does not contain either sulfur or nitrogen. It is biodegradable; it has low toxicity and does not corrode metals. In addition, DME is an important intermediate for the production of useful chemicals (i.e. methyl acetate and dimethyl sulfate) and petrochemicals (light olefins,

BTX aromatics). DME also provides a new competitive route for production of transportation fuels compared with the LNG technology or Fischer–Tropsch synthesis [4]. The DME produced from biomass (also called bio-DME) is a carbon-neutral fuel from the viewpoint of CO_2 emissions thus contributing to restrain the global warming.

1.1. Dimethyl ether synthesis

In the industry, DME manufacturing usually proceeds in two stages. The relevant reactions are displayed below [5,6]

$$CO_{(g)} + 2H_{2(g)} = CH_3OH_{(g)} \qquad \Delta H_0 = -90.4 \text{ kJ/mol}$$
$$2CH_3OH_{(g)} = CH_3OCH_{3(g)} + H_2O_{(g)} \qquad \Delta H_0 = -23 \text{ kJ/mol}$$

In the first stage, syngas is converted into methanol. The reaction involves copper based catalysts. The syngas conversion to methanol is limited by the thermodynamics, especially at high temperatures.

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In the second stage, methanol is dehydrated into DME over acid catalysts. The two-stage process is currently considered as the most mature route for DME synthesis. Methanol, however, is an expensive chemical feedstock, making the produced DME very costly.

The direct DME synthesis from syngas is an attractive alternative to the two-stage process. The direct DME synthesis, which proceeds on a single catalyst and in a single reactor, overcomes the thermodynamic constraints of methanol synthesis [5,7,8] leading to higher per-pass CO conversions and higher DME productivities. Note however that the water gas shift reaction which occurs under these conditions, results in significant CO_2 production:

$$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)} \qquad \Delta H_0 = -41 \text{ kJ/mol}$$
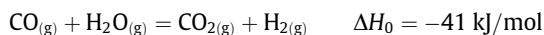
1.2. Bifunctional hybrid catalysts for direct DME synthesis

Direct DME synthesis requires highly efficient bifunctional catalytic systems which would combine a carbon monoxide hydrogenation function for methanol synthesis and an acidic function for methanol dehydration. The crucial issue in catalyst design could be therefore, optimization of the catalyst composition and interaction between these catalyst components [9]. Both well-dispersed copper particles with a high reducibility and large amounts of weak acidic sites are required for preparation of the bifunctional catalysts with satisfactory catalytic performance [10]. The hybrid catalysts for direct DME can be prepared using mechanical mixing of methanol synthesis catalyst and solid-acid catalyst, co-precipitation (sol–gel), impregnation or even more complex methods (e.g. capsule [11,12], core–shell catalysts [13]). It appears that strong interaction between hydrogenation and acidic functions in the catalysts prepared by impregnation and co-precipitation could lead to lower activity and poor stability.

The Cu–Zn–Al (CZA) catalyst for methanol synthesis has been successfully developed several decades ago. The advantages of the Cu/Zn systems include low cost and high selectivity to methanol. The catalyst composition has been carefully optimized in numerous reports [14–17]. Copper nanoparticles associated with a promoter, i.e. Zn, are usually considered as active phase for methanol synthesis. It is believed that in these nanoparticles copper can be either completely metallic [14] or partially oxidized under the reaction conditions. Other reports [18,19] suggest, however, that the specific interaction at the Cu/ZnO interface and stabilization of particular Cu morphologies may influence the catalytic performance.

Both carbon monoxide hydrogenation to methanol, methanol dehydration to DME and transport phenomena could be kinetically-relevant steps in direct DME synthesis. At the temperature characteristic of direct DME synthesis, carbon monoxide hydrogenation to methanol over copper based catalysts is a reversible catalytic reaction. Recently, major efforts have been dedicated to the design of methanol dehydration active phase in the bifunctional DME synthesis catalysts. The methanol dehydration occurs on an acid catalyst. Alumina has been first used [20–23] as an acid catalyst for methanol dehydration. The alumina-based catalysts, however, either pure or doped, are relatively sensitive toward deactivation by competitive adsorption of water and also by coke formation. The zeolite based catalysts have several advantages for methanol dehydration to DME in respect of more conventional alumina such as tunable acidity and better stability in the presence of steam [24,25]. The ZSM-5 zeolite has mostly been used as the acid component in bifunctional DME synthesis catalysts [26]. Other zeolites and microporous materials such as ferrierite [27], MCM-22, ITQ-2, IM-5, and TNU-9, polymeric Naflon resins [28], several microporous silicoaluminophosphates (SAPO-5, SAPO-11, SAPO-18 and SAPO-34) [29] and phosphorus modified γ-Al_2O_3 [30] have also been investigated. The catalytic performance of the zeolites for methanol dehydration was correlated with the concentration of Brönsted acid sites. In addition to zeolite acidity, other zeolite characteristics such as morphology and porous structure could be also important for the design of efficient catalysts. Composite catalysts for direct DME synthesis from syngas were prepared by Martínez et al. [31] using different zeolites (ZSM-5, FER, IM-5, TNU-9, MCM-22, ITQ-2). The authors attributed difference in the catalyst stability to different zeolite morphology. The ZSM-5 zeolite was found to be more efficient in direct DME synthesis than mordenite [32]. This was attributed to three dimensional pore system of ZSM-5 zeolite which may facilitate diffusion of reagents and reaction products.

The activity of the bifunctional catalysts decreases with time on stream due to the deactivation. The catalysts for direct DME synthesis have been susceptible to deactivation by copper oxidation, sintering [33,34], coke deposition [35,36] and contamination with impurities in syngas which could also affect the acid sites for methanol dehydration. Martínez and García-Trenco [37] attributed the deactivation to the detrimental interactions between the methanol synthesis catalyst and zeolite. The deactivation could be due to the interaction between Al species of zeolite and Cu sites of Cu/ZnO particles at the interface between these two components. Several attempts were made in the literature to improve the stability of these catalysts. Confining of copper nanoparticles within the zeolite matrix was proposed by Martínez and García-Trenco [37] as an efficient strategy to improve the catalyst stability in direct DME synthesis. It was found that the confined copper catalyst deactivated at a much lower rate than the catalysts prepared by mixing or grinding. Sierra et al. [38] attributed long-term catalyst deactivation to coking. Co-feeding with water attenuated coke deposition during the methanol synthesis. It was suggested that water partially inhibited the formation of coke precursors. Our recent report [39] showed that copper sintering, and copper migration leading to the decrease in the concentration of zeolite Brönsted acid sites could be major reasons for deactivation of copper zeolite catalyst prepared by kneading. Zeolite pre-treatment with tetraethyl orthosilicate can slow down [39] the catalyst deactivation and improve the DME productivity.

1.3. Zeolite particle sizes and catalytic performance

Zeolite is an important part of bifunctional catalysts for direct DME synthesis from syngas. The literature shows contradictory information about the effect of particle size on the performance of zeolite catalysts. The influence of zeolite particle sizes on the catalytic performance is often considered in relation to the zeolite shape selectivity [40–42]. The shape selectivity can be obtained by using the zeolite with channel dimensions approaching the sizes of the reacting molecules. This results in large differences in the diffusivity of linear and nonlinear isomers. A significant number of reports [43–47] have been dedicated to the evaluation of the zeolite particle size and molecular shape selectivity in hydrocracking reactions. No information is available however, about the effect of zeolite particle sizes on the catalytic performance of copper–zeolite catalysts in DME synthesis.

It is still not clear whether large or small zeolite particles could be optimal for this reaction. Jentoft et al. [45] found that the activity, selectivity and stability of the K-LTL zeolite-supported platinum catalysts in *n*-hexane reforming could be correlated with the ratio of the external surface area to the intracrystalline pore volume. Bonetto et al. [46] tested the beta zeolite with different crystal sizes in gas-oil cracking. The zeolite with the optimum crystallite size of 0.40 μm showed the best performance in terms of stability, activity and selectivity. The beta zeolite with a wide range of particle sizes was also tested as catalyst for degradation of high density polyethylene [47]. Zeolite nanoparticles with very large