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Feature Article

Single-step synthesis of dimethyl ether from biomass-derived syngas over CuO-ZnO-MO_x (M = Zr, Al, Cr, Ti)/HZSM-5 hybrid catalyst: Effects of MO_x

Yuxi Hua[a], Xiaoming Guo[a,*], Dongsen Mao[a], Guanzhong Lu[a], Garry L. Rempel[b], Flora T.T. Ng[b]

[a] Research Institute of Applied Catalysis, School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, PR China
[b] Department of Chemical Engineering, University of Waterloo, Waterloo N2L 3G1, Canada

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ABSTRACT

A series of CuO-ZnO-MO_x (M = Zr, Al, Cr, Ti) catalysts were prepared by co-precipitation method and characterized by ICP-OES, XRD, N_2 adsorption, N_2O titration, H_2-TPR, and XPS. The CuO-ZnO-ZrO_2 catalyst exhibits the highest BET surface area and Cu surface area. For all the CuO-ZnO-MO_x catalysts, Cu^0 was the predominant copper species detectable on the surface of both reduced and spent samples. As-prepared CuO-ZnO-MO_x catalysts were mixed physically with HZSM-5 zeolite to synthesize dimethyl ether (DME) via biomass-derived syngas. The highest CO conversion and DME yield were obtained over a CuO-ZnO-ZrO_2/HZSM-5 hybrid catalyst. The CO conversion increases with the increase in the Cu surface area, but the relationship between them is not linear. Due to the H_2-deficient characteristic of biomass-derived syngas, the water-gas shift reaction, by which H_2 can be produced in-situ for the hydrogenation of CO, plays an important role in the direct DME synthesis.

1. Introduction

Dimethyl ether (DME) is an important chemical intermediate for producing some valuable chemicals such as dimethyl sulfate, methyl acetate, methyl formate and lower olefins [1–3]. Since the physical and chemical properties of DME are similar to those of liquefied petroleum gas (LPG), it also can be used as a substitute for LPG [1,2,4]. To mitigate the problem of air pollution, recently, DME has gained attention as a clean alternative fuel for diesel engines due to its lower NO_x emission, lower particulates formation and less engine noise compared with the traditional diesel fuels [5].

It is well known that DME is synthesized commercially from syngas, which could be produced via coal gasification, natural gas reforming and biomass gasification [6–9]. Considering the fast depletion of fossil fuels and the impact of global warming, the route based on biomass gasification has been the most promising technology for producing syngas because biomass is a renewable energy resource and a carbon neutral fuel [10,11]. However, quite different from fossil-based syngas, biomass-derived syngas contains much more CO_2 but less H_2 (i.e. CO_2-rich and H_2-deficient) [7,12,13].

The traditional process for DME production from syngas is a two-step process. First, methanol is produced on a Cu-based catalyst via the hydrogenation of CO or CO_2, and then DME forms over a solid acid catalyst like γ-Al_2O_3 or ZSM-5 zeolite by the dehydration of methanol [14,15]. These two steps are carried out separately in different reactors. Lately, a single-step process was proposed and developed using the hybrid catalysts (Cu-based catalysts and solid acid catalysts) in one reactor for the direct production of DME [16,17]. With the single-step process, the methanol synthesis and methanol dehydration can be performed simultaneously, and the equilibrium limitation that exists for methanol synthesis could be easily overcome by the in situ dehydration of methanol [18].

To improve the catalytic performance of the hybrid catalysts for the DME synthesis, great efforts have been made to increase the copper dispersion of Cu-based catalysts [12,19–21], tune the acidic property of solid-acid catalysts [13,22–24], balance the two active sites (active sites for methanol synthesis and dehydration) [25] and promote the synergetic effects between the metallic and acidic catalysts [26–28]. As far as the methanol synthesis components of the hybrid catalysts are concerned, ternary catalysts containing Cu, Zn and an amphoteric oxide, are usually employed [29,30]. Apart from the most common CuO-ZnO-$A1_2O_3$ catalyst, many studies using CuO-ZnO-ZrO_2 and CuO-ZnO-TiO_2 as the methanol synthesis component for DME synthesis have been reported [12,22,31–33]. Although there are a few reports investigating the influence of the tertiary component amphoteric oxide on the properties of hybrid catalysts for DME synthesis via the fossil-base syngas, corresponding work for DME synthesis from the biomass-derived syngas is absent, to the best of our knowledge.

* Corresponding author.
E-mail address: guoxiaoming@sit.edu.cn (X. Guo).

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In this study, a series of CuO-ZnO-MO_x (M = Zr, Al, Cr, Ti) catalysts were prepared and used as the methanol synthesis component; HZSM-5 was chosen as the acidic component since it exhibited excellent performance for methanol dehydration [14,20]. These two components were then physically mixed and used for DME synthesis from biomass-derived syngas. The influence of MO_x on the properties of Cu-based catalysts and hybrid catalysts were emphasized. Also, noting the composition characteristic of biomass-derived syngas, the role of the water-gas shift reaction in the catalytic process was discussed.

2. Experimental

2.1. Catalyst preparation

The methanol synthesis component, CuO-ZnO-ZrO_2 (CZZ) catalyst with a nominal atomic ratio of Cu:Zn:Zr = 6:3:1 was prepared by a co-precipitation method. Specifically, an aqueous solution containing the respective metal nitrates ($Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Zr(NO)_4$) and a Na_2CO_3 solution were simultaneously added to the deionized water at 70 °C. The resulting suspension was stirred continuously and kept at pH = 7.0 by adjusting the relative addition rates of two solutions. After complete precipitation, the obtained precipitate was aged for 1 h. Then, the precipitate was filtered off and washed repeatedly with deionized water to remove residual sodium ions. The filter cake was dried at 110 °C for 12 h and subsequently calcined at 350 °C for 4 h. The CuO-ZnO-Al_2O_3 (CZA), CuO-ZnO-Cr_2O_3 (CZC) and CuO-ZnO-TiO_2 (CZT, with $TiCl_3$ as the Titanium source) catalysts were prepared using the same procedure. HZSM-5 with a Si/Al ratio of 38 was employed as the methanol dehydration component and purchased from the catalyst plant of Nankai University (China). CuO-ZnO-MO_x (CZM) and HZSM-5 were tableted separately and pulverized into granules (40–60 mesh). The hybrid catalysts were prepared by mixing physically CuO-ZnO-MO_x and HZSM-5 with a weight ratio of 4:1. All chemicals used were of reagent grade purity purchased from Shanghai Chemical Reagent Corporation, China.

2.2. Catalysts characterization

Elemental composition of the calcined catalysts was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), using a Thermo iCAP 6300 apparatus.

Powder X-ray diffraction (XRD) patterns of the sample were acquired on a PANalytical X'Pert instrument using Ni-filtered Cu Kα radiation at 40 kV and 40 mA. Two theta angles ranged from 20° to 60° with a speed of 6° per minute.

The BET specific area of the sample was determined by N_2 adsorption isotherms (−196 °C) on a Micrometrics ASAP–2020 M + C adsorption apparatus. The samples were evacuated at 200 °C for 6 h prior to N_2 dosage. The specific surface areas (S_{BET}) were calculated from the linear part of the Brunauer-Emmett-Teller (BET) plot.

Temperature-programmed reduction (TPR) measurements were performed in a linear quartz micro-reactor (i. d. 4 mm). 30 mg of sample was purged with N_2 at 300 °C for 1 h to remove adsorbed water and other contaminants. After cooled down to 50 °C, the catalyst was exposed to 10% H_2/N_2 (50 mL/min) at a heating rate of 5 °C/min up to 300 °C. H_2 consumption was monitored by a thermal conductivity detector.

The copper surface area (S_{Cu}) was determined by N_2O titration using a six-way valve equipped with a sample loop. About 0.2 g of sample was loaded into a linear quartz micro-reactor (i. d. 4 mm) and reduced in a 10% H_2/N_2 gas mixture at 300 °C for 1 h. After the reduction, the sample was purged with He and cooled down to the reaction temperature (60 °C). Then, a sample loop of 2 vol% N_2O/He gas mixture was intermittently fed into the reactor. The N_2 produced by the decomposition of N_2O on the exposed Cu atoms was detected using a mass spectrometer (Pfeiffer Vacuum Quadstar, 32-bit). The metallic copper surface area was calculated assuming an atomic copper surface density of 1.46×10^{19} atoms/m^2 and a stoichiometry of $N_2O/Cu = 0.5$ [34].

The X-ray photoelectron spectroscopy (XPS) and X-ray-induced Auger electron spectroscopy were recorded on an ESCALA 250 Xi spectrometer, using a standard Al K_α X-ray source (1486.6 eV). The energy analyzer was set to a pass energy of 30 eV. The binding energy (BE) values were referenced to the adventitious C 1 s peak (284.6 eV). Quantification of the surface atomic concentrations was carried out using the sensitivity factors supplied for the XPS instrument. The XPS instrument was equipped with a reaction chamber with controlled atmosphere and temperature, in which the catalyst samples could be treated under different conditions. The samples were transferred between the reaction chamber and analysis chamber by a transfer rod under ultrahigh vacuum.

NH_3-TPD experiments for the surface acidity determination were performed using a conventional flow apparatus equipped with a thermal conductivity detector. In a typical analysis, 100 mg of the sample was loaded into a linear quartz micro-reactor and pretreated in a 10% H_2/N_2 gas mixture at 300 °C for 1 h. The sample was cooled down to 50 °C and then exposed to NH_3 for 30 min. Then, the sample was purged with N_2 at 100 °C for 1 h to remove the physisorbed NH_3. The TPD measurements were conducted in flowing N_2 (30 ml/min) from 100 to 550 °C with a constant heating rate of 10 °C/min.

2.3. Catalytic activity measurement

The catalytic activity test was performed in a continuous-flow, fixed-bed reactor. Typically, 0.5 g of catalyst diluted with quartz sand (both in 40–60 mesh) was packed into a stainless steel tubular reactor (5 mm i. d.). Prior to each test, the catalyst was reduced in-situ in a 10% H_2/N_2 stream (30 mL/min) at 300 °C for 3 h under atmospheric pressure. Then, the reactor was cooled to 160 °C, and the biomass-derived syngas ($H_2/CO/CO_2/N_2$ = 36/36/18/10, molar) was introduced, raising the pressure to 3.0 MPa and the temperature to a given temperature. All post-reactor lines and valves were heated to 150 °C to prevent product condensation. The product stream was analyzed by an online-GC (7820A, Agilent) equipped with a TCD (for CO, CO_2, and CH_4 analysis) and a FID (for DME, methanol, and other hydrocarbons analysis). The CO and CO_2 conversion, product selectivity and DME yield were calculated using the formula given in Ref [19].

3. Results and discussion

3.1. Structural and textural properties

The chemical compositions of the calcined CZM catalysts determined by ICP-OES are presented in Table 1. The compositions of CZM catalysts generally agree with the nominal compositions calculated for catalyst preparation, and a ratio of Cu/Zn is about 2.1 for all samples.

The XRD patterns of the calcined CZM catalysts were collected and presented in Fig. 1(a). The diffraction peaks at 2θ of 35.6°, 38.8° are identified as CuO phase (PDF #48-1548), and the diffraction peaks at 31.7°, 34 .5°, 36.2°, 47.5° and 56.6°are assigned to the phase of ZnO (PDF #36-1451). There is no distinct diffraction peak of MO_x (M = Zr, Al, Cr and Ti) crystallite for the corresponding catalyst. This indicates

Table 1
Chemical composition of the calcined CZM catalysts.

Catalyst	Metal content (mol %)			Cu/Zn atomic ratio
	Cu	Zn	M	
CZZ	61.3	29.8	Zr: 8.9	2.06
CZA	60.6	28.6	Al: 10.8	2.12
CZC	61.9	29.6	Cr: 8.5	2.09
CZT	59.9	28.8	Ti: 11.3	2.08