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Full Length Article

An investigation into the effects of different existing states of aluminum isopropoxide on copper-based catalysts for direct synthesis of dimethyl ether from syngas

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ABSTRACT

Aluminum isopropoxide (AIP) is a vital raw material to produce high surface area alumina catalyst, which is used for catalytic applications, such as hydrocracking, Fischer-Tropsch and STD (syngas to dimethyl ether) reactions. However, the different existing states have an effect on hydrolysis and condensation in the process of precursor preparation. The Cu/Zn/Al slurry catalysts were prepared by aluminum isopropoxide, which were liquid state, crystalline state and solid state, utilizing a complete liquid phase preparation technology. In the dimethyl ether (DME) synthesis reaction, the aluminum resource of crystalline state was prepared for slurry catalyst, which presented high CO conversion and DME selectivity of 54.32% and 69.74%, respectively. Characterization results indicated that different forms of AIP have the variant coordination numbers of Al-O and polymerization degrees, and the catalyst prepared by crystalline state consists amount of tetra-coordinated Al and few hexa-coordinated Al, which can exert different hydrolysis and condensation process compared with other aluminum sources, and finally it contributes to the strong interaction between active site copper species and Zn/Al species, confirming more Cu^{+} is responsible for the synthesis of DME in the slurry reactor.

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1. Introduction

Due to the ever-growing world need for energy and the growth in global population, the development of alternative resources and more sustainable technologies becomes a great challenge for science and technology in the imminent decades [1,2]. As a result of the simplest ether without a C—C bond in the formula, dimethyl ether (DME) is one of the popular research fields in environmental chemistry and energy chemistry [3]. DME can replace LPG (liquefied petroleum gas) due to its similar physicochemical property. Moreover, with the high cetane number between 55 to 60 and lower auto-ignition temperature of 235 °C, it usually can be used as diesel fuel, and it has with absolutely low soot emission in the waste gas from a diesel engine [4,5]. Hence, as a substitute common fuel, it is very secure and friendly to the environment [6].

The process of DME synthesis is strong exothermic reaction, including three consecutive processes, which are methanol formation, methanol dehydration, and water-gas shift reaction [7]. The direct synthesis of DME from syngas includes methanol synthesis and methanol dehydration processes, both in one step on the surface of a bi-functional catalyst. Compared with the fixed bed reactor, the slurry phase reactor has a lot of advantages on the highly exothermic reactions, and it is apt to remove the strong heat by the existence of a liquid medium to attain nearly isothermal situation [8–10].

It is well known that aluminum has two significant roles of methanol formation and methanol dehydration in the direct syngas to DME (STD) reaction [2,7]. Some researchers have studied the preparation of alumina materials with proper properties such as surface area, pore volume, particle size, and pore diameter by aluminum isopropoxide [11–13]. Besides, aluminum isopropoxide is widely used as the raw material to produce aluminum sol-gel resulting from liable to be purified by distillation, and to be hydrolyzed [14,15]. The research by Huang et al. [16] investigated the modified aluminum isopropoxide in the catalyst preparation

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process, which can influence obviously the catalyst performance for the production of dimethyl ether in the slurry bed.

According to some literatures reported, it was found that the AIP can show different existing states with the ageing time [17–19]. The different states of AIP were hydrolyzed to produce hydrated oxides with different rates in the process of sol-gel. Since 1975, Yoldas [20] used aluminum isopropoxide as raw material to control hydrolysis for aluminum sol, the method has been used by many people. Previous studies [21–24] paid more attention to the reaction parameters of preparing sol, such as the reaction temperature, reaction time, pH value, additives, peptizators and H_2O/AIP ratio. However, no opinions were focused on the sol prepared by AIP itself with different existing forms, which were found in the process of homemade AIPs. Our group put forward a novel catalyst preparation technology named Complete Liquid-phase Preparation Technology applied for slurry bed reactor [25]. This method could simplify the conventional drying and calcination procedures of slurry catalyst prepared from metallic salt solution to the slurry catalyst. Based on this technology, the Cu/Zn/Al catalysts were prepared with different existing states of AIP, which were made by our laboratory, for the one-step direct synthesis of DME from syngas in a slurry bed reactor. The effects of different existing states of AIP (liquid state, crystalline state and solid state) on the catalysts performance for DME synthesis were investigated. This work and obtained results in the present research not only provide a comprehensive cognition on polymerization degree of AIP with the time goes by, but also are conducive to realize the relationship between the structure of the catalysts and the catalytic performance.

2. Experimental

2.1. Catalyst preparation

The catalyst preparation was divided into three stages:

2.1.1. Stage 1: Preparation of aluminum isopropoxide

Aluminum powder was added to superfluous isopropyl alcohol at 355 K for 1 h, then raise the temperature to 365 K for 10 h with stirring. Subsequently, perform the vacuum distillation to eliminate the un-reacted isopropyl alcohol at a low temperature. Then get the viscous AIP from the mixed liquid by vacuum distillation at a high temperature. As the time goes by, fresh AIP will exhibit different existing forms, such as liquid state, crystalline state and solid state. Then the three states of AIP were applied to prepare the Cu/Zn/Al slurry catalysts.

2.1.2. Stage 2: Preparation of sol-gel

The hybrid of $Cu(NO_3)_2{\cdot}3H_2O$ (36.24 g), $Zn(NO_3)_2{\cdot}6H_2O$ (22.35 g) and anhydrous ethyl alcohol (50 mL) was added to the flask. Then 61.28 g $(C_3H_7O)_3Al$,which was got from Stage 1, and was added to the Cu/Zn solution. The 260 mL distilled water flowed into the flask at the rate of 10 mL/min by the peristaltic pump, and then the solution was mixed by stiring for 1 h at 358 K to achieve hydrolysis of AIP. Subsequently, the solution was allowed to stir for 6 h to get the sol under reflux. Then, the sol was further reacted to a blue gel after eight days ageing time at room temperature.

2.1.3. Stage 3: Preparation of slurry catalysts

The prepared gel in stage 2, liquid paraffin and Span80 were added to a three mouths round bottom flask. Then the mixture was heated from room temperature to 553 K with a heating rate 2 K/min, and then it was maintained for 8 h at temperature of 553 K. At the same time, a flow (N_2) of 40 mL/min was brought into the flask at normal pressure. After the treatment, a slurry catalyst was acquired. In order to being convenient, three catalysts are noted according to the state of AIP, being liquid state, crystalline state and solid state, then the catalysts are named CZ-LA, CZ-CA and CZ-SA, respectively.

2.2. Characterization of catalysts

Due to the paraffin covered on the surface of the catalysts, extraction with the petroleum ether was used to gain the actual properties, and then dry these catalysts at the room temperature before tests. ^{27}Al nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-III 400 spectrometer with a ^{27}Al frequency of 130.4 MHz. The XRD profiles of these catalysts were recorded on a Rigaku D/max 2500 diffractometer (40 kV, 100 mA, Cu Kα radiation). H_2-TPR data of the catalysts were received on a temperature programmed adsorption reactor of TP-5000 made in Tianjin Xianquan Corporation. 0.05 g catalyst was used in the device and heated to 813 °C at the rate of 10 °C/min in a N_2 atmosphere, including 5% of H_2 at a flow rate of 30 mL/min, using a thermal conductivity detector (TCD) to monitor the hydrogen consumption and reduction peaks. In order to obtain the accurate quantity of hydrogen consumption, 20 mg Ag_2O was chosen as a reference. X-ray photoelectron spectroscopy (XPS) information was acquired with Al Kαradiation (1486.6 eV) on a type of AXIS ULTRA DLD apparatus of Kratos in England. It employs Al Kα of 1486.6 eV as the radiation and the vacuum of the analytical chamber was at least 7.0×10^{-8} Pa. Binding energy (BE) was calibrated with carbon 1 s 284.8 eV, which make BE with an accuracy of ±0.1 eV. The BET surface area, total pore volume and average pore diameter of the catalysts were obtained by nitrogen adsorption and desorption isotherm at −196 °C using a Quantachrome SI series equipment. The catalysts were degassed in vacuum at 210 °C for 4 h before measurement. According to the BET and BJH formula, specific surface area and pore volume, pore size distribution of the catalysts are calculated respectively.

2.3. Catalytic activity test

The one-step DME synthesis reaction was taken place in a 500 mL slurry bed reactor with a mechanical magnetic agitator at the rate of 1000 rpm/min. The Cu/Zn/Al slurry catalyst was reduced in gas mixture of 20% H_2 and 80% N_2 under the normal pressures at 280 °C for 10 h before the reaction. Then, the syngas of total flow rate 100 mL/min (H_2/CO = 1:1) was brought into the reactor under 4.0 MPa, and the temperature was programmed at a rate of 2 °C/min to 280 °C, with overall gas hourly space velocity of 350 mL/(g_{cat}·h). The products were analyzed on-line on a GC-950 gas chromatograph equipped with a flame ionization detector (FID), a thermal conductivity detector (TCD) and methane conversion oven. The volume fraction of each component was calculated by correlation method, which is used methane as an internal standard. The results of CO conversion and selectivity of DME were informed by the carbon balance. The products were evaluated after the beginning of the reaction of 24 h.

3. Results and discussion

3.1. Structures of aluminum isopropoxide with different existing states

Two factors determined the structures of aluminum alkoxy compounds. On the one hand, the propensity for the metal to attain its maximum coordination number, which results in polymeric systems. On the other hand, since the steric hindrance factor, the alkoxy group is limited to increase the size in the polymeric system. Effectively, the two effects are finely balanced when it comes to aluminum isopropoxide [26]. In order to investigate the different coordination numbers of Al-O in the different existing forms of

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