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The facile preparation of Cu–Zn–Al oxide composite catalysts with high stability and performance for the production of dimethyl ether using modified aluminum alkoxide

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ABSTRACT

Modified aluminum alkoxide prepared by alcoholysis was used as an aluminum source in the complete liquid-phase technology for the preparation of slurry catalysts. The use of the modified aluminum alkoxide afforded control over the rate of the hydrolysis/condensation reactions during the preparation of the catalyst precursors, thereby generating catalysts with a fine nano-structured active metal and metallic oxide particles. Four types of Cu–Zn–Al (molar ratio is 2:1:4) catalysts were prepared using different procedures. These catalysts were tested for CO hydrogenation at 553 K, 4.0 MPa and $H_2/CO = 1.0$ in a kettle with a mechanical agitator. The results indicated that the activity of the catalysts was greatly dependent on the rate of the hydrolysis/condensation reactions, and the catalyst with the best catalytic performance was obtained by controlling the hydrolysis/alcoholysis rate during catalyst synthesis by pre-alcoholysis of AIP as the aluminum source, over which the CO conversion and dimethyl ether selectivity could reach 62.6% and 62.5%, respectively.

Introduction

Dimethyl ether (DME) is an excellent clean burning transportation fuel alternative for compression ignition engines and also an excellent fuel for household purposes [1–3]. The catalytic conversion of syngas, derived from coal and natural gas, into DME is one of the most promising routes to obtain an alternative clean energy source.

Traditionally, DME can be produced through two methods. One is methanol dehydration on a single solid acid catalyst such as γ-alumina or HZSM-5 zeolite [4–6], where the methanol is separately made from syngas, and another is a couple of consecutive reactions for DME direct synthesis from syngas on a hybrid catalyst, where the hybrid catalyst is a simple mixture of methanol synthesis catalyst and methanol dehydration catalyst. Direct synthesis of DME from syngas (STD process) is a promising process because of its significant economic value and theoretical importance. The key steps in the STD process are supposed to be methanol synthesis, methanol dehydration, and the water gas shift (WGS) reaction.

$$2CO + 4H_2 \rightarrow 2CH_3OH \tag{1}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{2}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{3}$$

The combination of reactions (1)–(3) gives the overall reaction:

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \tag{4}$$

Since methanol formed by reaction (1) is consumed for the formation of DME and water in reaction (2). The water generated in reaction (2) is shifted by the WGS reaction (3), forming carbon dioxide and hydrogen; the latter is a reactant for the methanol synthesis in reaction (1). Thus, one of the products of each step is a reactant for another. This creates a strong driving force for the overall reaction, allowing very high syngas conversion in a single pass. Additionally, the one-step direct synthesis of DME in a slurry reactor has many merits in caloric transfer, energy utility, and online catalyst substitution when compared with operation in a

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fixed bed reactor. However, catalyst deactivation toward direct DME synthesis in a slurry reactor has yet to be efficiently overcome, even in a fixed bed reactor. As such, our group reported a novel technology for the preparation of slurry catalysts coined "complete liquid-phase technology", which prevents catalyst deactivation [7]. However, the resulting catalyst activities are not as satisfactory as those prepared by conventional methods such as co-precipitation and impregnation. Although excellent progress has been accomplished [8–10], only some studies reported the long-term stability of the catalysts. Thus, catalyst deactivation remains a limitation factor in this field. In the present work, the complete liquid-phase technology is remarkably improved to greatly promote catalyst activity.

The use of precursor for catalyst preparation by the sol–gel method can afford better control over the grain size and porosity of the formed catalyst precursor compared with conventional precipitation, where these parameters are very difficult to control [11–13]. However, using the sol–gel technology, molecular distribution can only be obtained under ideal hydrolysis/condensation conditions. Rapid hydrolysis and condensation reactions lead to prompt formation of dense inorganic networks and uncontrolled phase separation between the organic and inorganic components [14]. There are many common means to limit hydrolysis and condensation reactions [15–21].

According to the principle of sol–gel synthesis, there exist facile methods to modify the metal alkoxide in the sol–gel system using alcohols and in the absence of other chemical additives. Livage et al. [22] reported that sol–gel synthesis can be described by alcoholic permutation (alcoholysis), hydrolysis, and condensation reactions. The alcoholic permutation reaction is also called alcoholysis reaction. Thus, alkoxide reactivity toward hydrolysis/condensation may easily be modified by changing the solvent. Metal alkoxide reacts with a variety of alcohols to set up the following type of equilibrium:

$$M(OR)_n + xR'OH \rightarrow M(OR)_{n-x}(OR')_x + xROH$$

Hydrolysis and condensation reactions follow the equations:

$$M(OR)_n + xH_2O = M(OH)_x(OR)_{n-x} + xROH \cdots M(OH)_n$$

$$-M-OH + HO-M- = -M-O-M- + H_2O$$

$$-M-OR + HO-M- = -M-O-M- + ROH$$

It is also well known that the hydrolysis of an alkoxide strongly depends on the length of the alkyl chain [23]. Thus, it should be possible to adjust the rate of gelation of a given alkoxide using alcohols with different alkyl chain lengths to achieve homogeneous oxide complexes that are suitable for catalyst preparation.

In this work, a series of experiments were designed to adjust the hydrolysis/condensation rate in the sol-forming process. The findings highlight that using aluminum alkoxide modified by alcoholysis as an aluminum source in the preparation of precursors generated slurry catalysts with high activity and stability.

Experimental

Preparation of bifunctional slurry catalysts

The components for methanol synthesis and methanol dehydration of Cu–Zn–Al bifunctional catalysts were prepared in one-pot, and the Cu/Zn/Al atomic ratio of the catalyst is 2:1:4. The amounts of $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and aluminum isopropoxide (AIP) used were 36.24, 22.31, and 61.28 g, respectively. Ethanol (EtOH), water, and polyethylene glycol 600 (PEG600) were used as solvent, hydrolyzing agent, and surfactant, respectively. The molar ratios used for the synthesis were H_2O/AIP = 50, EtOH/AIP = 35, and HNO_3/AIP = 0.3. A series of catalysts were designed using different methods, involving water and alcohol as solvents and pre-alcoholyzed AIP to carefully adjust the rate of the hydrolysis/condensation reactions. Method 1 is referred to as direct hydrolysis. AIP was slowly added to distilled water (240 mL), which contained dissolved $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and PEG600 (2.6 g). The reaction mixture was maintained at 358 K for 1 h in a water bath for hydrolysis. Then, dilute HNO_3 (4.5 mL) was added dropwise to the solution and stirred under reflux for 6 h at 368 K. Method 2 involves the use of ethanol as solvent for the alkoxide. AIP powder was dissolved in ethanol (150 mL) at room temperature, after which the suspension was added to the $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and PEG600 aqueous solution, then kept at 358 K for 1 h and stirred under reflux for 6 h at 368 K after adding the dilute HNO_3. Method 3 is referred to as the pre-alcoholysis route. AIP powder was slowly added to ethanol solution and stirred vigorously under reflux for 2 h at 348 K and aged for 1 day. The solution obtained was added to the aqueous solution containing $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and PEG600. The remaining steps were the same as those used in Method 2. In Method 4, the solution obtained by pre-alcoholysis and ageing for 1 day was slowly added to the mixed ethanol solution containing $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and PEG600. After that, distilled water was added dropwise, and the obtained solution was maintained at 358 K for 1 h. Dilute HNO_3 was then added dropwise to the solution and stirred under reflux for 6 h at 368 K.

Using the methods described above, a homogeneous sol was obtained. The sol was placed at room temperature and aged for several days. The sol–gel was dispersed in paraffin (300 mL) under mechanical stirring and heated from room temperature to 553 K in N_2 flow and maintained at this temperature for 8 h. The slurry catalysts were subsequently obtained. For convenience, catalysts are denoted in accordance to the method adopted for preparation of the precursor, as described above, i.e. catalysts are referred as Cat1, Cat2, Cat3, and Cat4.

Characterization

In order to eliminate the effect of paraffin on catalyst characterization and show the actual property of the slurry catalyst, the slurry catalysts were extracted by petroleum ether and dried at room temperature before characterizations.

X-ray diffraction (XRD) data of fresh and used catalysts were collected on a Rigaku D/max 2500 power diffractometer (Cu $K\alpha$ radiation, 40 kV, 100 mA). The phase identification was made by using the Joint Committee on Powder Diffraction Standards files (JCPDS).

The BET surface areas and pore volume of samples were calculated from the nitrogen adsorption–desorption isotherm obtained at 77 K measured by a Micromeritics ASAP 2020. H_2-TPR was carried out in a laboratory-made microreactor.

For each TPR experiment, the catalyst was packed into the reactor and heated to 783 K at the rate of 10 K/min in a stream of H_2/N_2 (5/95) at a flow rate of 30 mL/min, using a thermal conductivity detector to record the reduction peaks. Copper surface area and dispersion were measured using a N_2O decomposition method on the same apparatus as that employed for the H_2-TPR test. The catalysts (0.1 g) were first reduced upon heating to 350 °C in a 10% H_2/N_2 mixture with a ramp of 10 °C/min, and the temperature was maintained for 1 h. The amount of hydrogen consumed is denoted as A_1. Then, the reduced samples were cooled to 30 °C and purged with N_2 for 30 min. The samples were exposed to N_2O at 30 °C for 20 min to oxidize surface copper to Cu_2O and then flushed with N_2 to remove the N_2O. Finally, TPR