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Effect of H_2O on Cu-based catalyst in one-step slurry phase dimethyl ether synthesis

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ABSTRACT

One-step dimethyl ether (DME) synthesis in slurry phase was catalyzed by a hybrid catalyst composed of a Cu-based methanol synthesis catalyst and a γ-Al_2O_3 methanol dehydration catalyst under reaction conditions of 260 °C and 5.0 MPa. It was found that instability of the Cu-based catalyst led to rapid deactivation of the hybrid catalyst. The stability of the Cu-based catalyst under DME synthesis conditions was compared with that under methanol synthesis conditions. The results indicated that harmfulness of water, which formed in DME synthesis, caused the Cu-based catalyst to deactivate at a high rate. Surface physical analysis, elemental analysis, XRD and XPS were used to characterize the surface physical properties, components, crystal structures and surface morphologies of the Cu-based catalysts. It was found that Cu^0 was the active component for methanol synthesis and Cu_2O might have less activity for the reaction. Compared with methanol synthesis process, crystallite size of Cu became bigger in DME synthesis process, but carbon deposition was less severe. It was also found that there was distinct metal loss of Zn and Al caused by hydrothermal leaching, impairing the stability of the catalyst. In slurry phase DME synthesis, a part of Cu transformed into $Cu_2(OH)_2CO_3$, causing a decrease in the number of active sites of the Cu-based catalyst. And some ZnO converted to $Zn_5(OH)_6(CO_3)_2$, which caused the synergistic effect between Cu and ZnO to become weaker. Crystallite size growth of Cu, carbon deposition, metal loss of Zn and Al, formation of $Cu_2(OH)_2CO_3$ and $Zn_5(OH)_6(CO_3)_2$ were important reasons for rapid deactivation of the Cu-based catalyst.

1. Introduction

Dimethyl ether (DME) has been widely known as clean alternative fuel due to its similar physical properties with liquefied petroleum gas (LPG) [1–3]. DME has a higher cetane number (55–60) and has been studied as an alternative for diesel fuel [4–6].

DME can be synthesized from methanol dehydration using acid catalyst. Recently, one-step synthesis of DME from syngas has attracted more and more industrial interests [7–9] because of lower thermodynamic limitation and investment. The one-step process mainly consists of three reactions:

$$CO + 2H_2 \Leftrightarrow CH_3OH - 90.4KJ \quad (1)$$

$$2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O - 23.4KJ \quad (2)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 - 40.9KJ \quad (3)$$

The reactions (1) and (3), representing methanol synthesis reaction and water–gas shift reaction respectively, are catalyzed by Cu-based methanol synthesis catalyst (MSC). The reaction (2) is catalyzed by methanol dehydration catalyst (MDC) such as γ-Al_2O_3 and ZSM-5. MSC and MDC make up hybrid catalyst for DME synthesis by mixing them together mechanically. Because methanol synthesis reaction, methanol dehydration reaction and water–gas shift reaction are all exothermic reactions, one-step DME synthesis is a highly exothermic process. Traditionally, one-step process is carried out in a fixed bed reactor. But fixed bed reactor is not suitable for this process for its limited heat removal capacity. Slurry reactor is an ideal reactor for DME synthesis [10–12], for it has many advantages such as better heat transfer performance, lower investment and so on. Though one-step DME synthesis in slurry reactor has many merits, the hybrid catalyst deactivates at a high rate [13]. Consequently, slurry phase DME synthesis has not been widely applied to industrial production yet.

Since the hybrid catalyst is composed of MSC and MDC, deactivation of either the MSC or MDC can cause the hybrid catalyst to deactivate. Therefore, it is appropriate to investigate the deactivation behavior of each catalyst separately under one-step DME synthesis conditions. In previous paper [14], the stability of Cu-based catalyst in methanol synthesis conditions and the stability of γ-Al_2O_3 catalyst in methanol dehydration conditions had been studied respectively. But the reaction atmosphere of one-step DME synthesis is very different from that of methanol synthesis and methanol dehydration. Only a negligible amount of water is produced through reversed water–gas shift reaction in methanol synthesis, while more water appears in DME synthesis because of the existence of methanol dehydration

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reaction coupled with reversed water–gas shift reaction. Therefore, the hybrid catalyst for one-step DME synthesis is in an atmosphere where an amount of water and syngas co-exist. In order to investigate the catalytic stability of the hybrid catalyst, MSC and MDC separately under one-step DME synthesis atmosphere as same as possible, three modes was specified in the experimental section of this paper. The stability test of MSC was carried out with a given amount of water co-fed into the methanol synthesis system in Mode 2. The composition ratio of syngas and water was calculated according to a mathematical modeling of equilibrium DME synthesis system [15]. Analogously, the stability of MDC was tested with a given amount of syngas and methanol co-fed into the methanol dehydration system in Mode 3, simulating one-step DME synthesis atmosphere of Mode 1.

In this paper, the deactivation reasons of the hybrid catalyst in slurry phase were studied by comparing the textual and structural properties of the Cu-based catalyst samples which were obtained from different reaction modes. Some valuable conclusions were obtained, which had not been reported before.

2. Experimental section

2.1. Catalytic activity tests

In order to obtain the deactivated catalyst samples with different reaction experiences, three reaction modes were defined as:

Mode 1: DME synthesis using hybrid catalyst, which was prepared by physically mixing C301 MSC (Taiyuan Chemical Fertilizer Plant, Shanxi, China) and γ-Al_2O_3 MDC (Shanghai Hengye Chemical Engineering Co., Ltd), and syngas as reactant.

Mode 2: Methanol synthesis using C301 MSC as catalyst and syngas as reactant, water was co-fed with syngas to simulate the reaction atmosphere of Mode 1. A high pressure liquid pump was used to add the water into the reactor. For comparison, some reaction was conducted without water addition.

Mode 3: Methanol dehydration using γ-Al_2O_3 MDC as catalyst and methanol as reactant, syngas was co-fed to simulate the reaction atmosphere of Mode 1. Methanol was introduced into the reactor by the same high pressure liquid pump used in Mode 2.

All of the catalyst stability tests were carried out in a 250 mL mechanically agitated slurry autoclave reactor, in which poison-removed liquid paraffin (80 mL) was used as solvent. For Mode 1 and Mode 2, the catalysts (C301 4 g + γ-Al_2O_3 2 g, 200–250 mesh for Mode 1; C301 4 g, 200–250 mesh for Mode 2) were reduced in the slurry reactor by diluted hydrogen (10% H_2 + 90% N_2) at 260 °C for 16 h, which was approached at a given programmed temperature rising rate. After reduction, syngas ($H_2/CO \approx 2$), controlled by a high-pressure mass flow meter (Brooks 5850E, USA), was introduced into the reactor under pressure of 5.0 MPa. For Mode 3, γ-Al_2O_3 powder (2 g, 200–250 mesh) was mixed with liquid paraffin (80 mL) and filled in the autoclave. The catalyst was heated to 260 °C at the same rising rate as Mode 1 and Mode 2. Then a given proportion of methanol and syngas was co-fed into the reactor. Reaction conditions for all operation modes were 260 °C, 5.0 MPa and gas space velocity was 4000 h^{-1}.

The analysis of effluent products was described elsewhere [16].

For characterization of the Cu-based catalyst after reduction or after reaction, Ar was used to protect the samples, which was filtrated and washed with ether to remove the liquid paraffin.

2.2. Surface physical property analysis

BET surface area, total pore volume and average pore diameter of the Cu-based catalysts were determined by nitrogen adsorption–desorption isotherm at −196 °C using a Micromeritics Tristar 3000 apparatus (USA). Prior to measurement, the samples were degassed in vacuum at 200 °C for 5 h. Barrett–Joyner–Halenda (BJH) method was applied to measure the pore size distribution.

2.3. Elemental analysis

Elemental composition of C and O in the Cu-based catalysts was determined by Vario EL element analyzer (Elementar, Germany). Elemental composition of Cu, Zn and Al was measured by inductively coupled plasma with atomic emission spectroscopy (ICP-AES), using an Atomscan 16 apparatus (TJA, USA).

2.4. X-ray diffraction (XRD)

Powder X-ray diffraction patterns were recorded using a Rigaku Dmax-rA X-ray diffractometer with CuNi radiation at 40 kV and 40 mA, graphite monochromator. Two theta angles ranged from 5° to 80° with a speed of 5° per minute and step length of 0.02°. The crystallite size of Cu was calculated from XRD spectra by using Debye–Scherrer equation, taking into account an apparatus line broadening.

2.5. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES)

X-ray photoelectron and X-ray excited Auger spectra were obtained with an AXIS Ultra electron spectrometer from Kratos Analytical. The spectrometer utilized monochromatized Al Kα ($h\nu = 1486.6$ eV). The anode was operated at a power of 196 W (14 kV, 14 mA). During the experiments, the analysis chamber was regulated below 1.33×10^{-6} Pa. Binding energies (BE) were corrected using contamination carbon 1s 284.8 eV as an internal reference, which gave BE-values with an accuracy of ±0.1 eV.

3. Results and discussion

3.1. Catalyst stability tests

The catalytic stability of the hybrid catalyst, MSC and MDC are compared in Fig. 1. Methanol conversion declined slowly from 50.5% to 46.2% after 192 h methanol dehydration reaction. On the contrary, CO conversion declined rapidly from 43.5% to 27.0% in methanol synthesis reaction and 52.6% to 33.7% in DME synthesis reaction, respectively. Deactivation rates of the MSC and the hybrid catalyst were very close. This implies that rapid deactivation of the hybrid catalyst was caused by deactivation of the MSC, not the MDC.

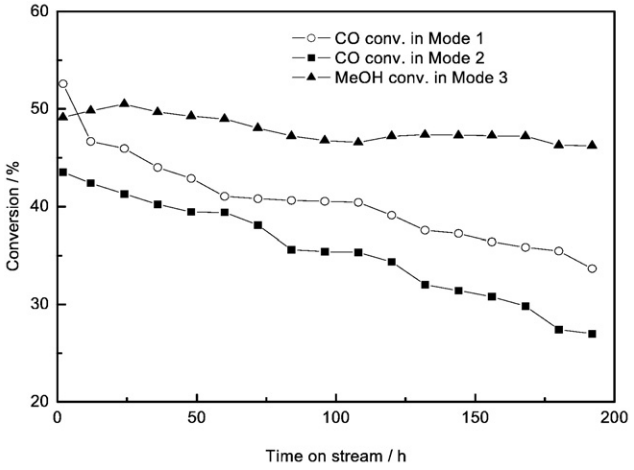

Fig. 1. Stability tests of the catalysts. Reaction conditions: $H_2/CO = 2$, 260 °C, 5.0 MPa, 4000 h^{-1}. Mode 2: H_2O/syngas = 0.1 (mol/mol). Mode 3: MeOH/syngas = 0.15 (mol/mol).