

Core-shell structured CuO–ZnO@H-ZSM-5 catalysts for CO hydrogenation to dimethyl ether

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ABSTRACT

A series of core-shell structured CuO–ZnO@H-ZSM-5 (CZ@H) catalysts were prepared by homogeneous precipitation through urea hydrolysis. This novel preparation procedure and excellent core-shell structure had contributed to its high-performance for CO hydrogenation under 260 °C, 2.0 MPa and high space velocity (6000 mL/(g_{cat} h)). The space time yield of dimethyl ether (DME) over CZ@H(7.5) reached 0.76 g_{DME}/g_{cat} h with a 69.6% selectivity, and these values exceeded that of hybrid catalyst prepared by traditional mixing method (0.37 g_{DME}/g_{cat} h, 65.1% selectivity of DME). This high performance of bifunctional CZ@H catalysts could be attributed to the high Cu dispersion and well-defined core-shell structure.

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1. Introduction

Dimethyl ether (DME) has been utilized as alternate fuel for vehicle engines instead of diesel, and as fuel additive and family cooking gas instead of liquefied petroleum gas (LPG) [1]. Compared with the traditional chlorofluorocarbon (CFCs, Freon) and newer R-134a (HFC-134a), DME and fluoro-dimethyl ether are also widely used in environmental friendly aerosol spray and green refrigerant because of their zero ozone depletion potential (ODP) and lower globe warming potential (GWP) [2]. Catalytic conversion of synthesis gas (syngas) derived from coal, biomass, and natural gas to DME is one of the most promising routes to obtain an alternative clean energy source [3].

The single-step DME synthesis (STD) from syngas involves methanol synthesis, methanol dehydration and water–gas shift reactions, in which a bifunctional catalyst, usually including methanol synthesis catalyst and methanol dehydration catalyst, is used. Compared with the two-step process, the most advantage of STD process lies in its simplicity as only one fixed bed or a slurry reactor is used. And the STD process is a tandem reaction in which methanol synthesis and its dehydration performed consecutively, this creates a strong driving force for the overall reaction and enhances the conversion of syngas [4]. According to this mechanism, the integration of CO hydrogenation sites and methanol dehydration

sites, and the structure of the bifunctional catalysts are of great importance for this process.

Numerous methods have been tried to prepare a sufficient bifunctional catalyst, and the most common one is direct mechanically mixing of methanol synthesis catalyst (Cu-based catalysts) and dehydration catalyst (γ -alumina, zeolites et al.) [4–7]. Other methods, such as co-precipitation and impregnation, are also reported widely in preparing of these bifunctional catalysts. But these methods are always pH-sensitive, time-consuming and restricted by the deviation from stoichiometry [8–10]. Because of these drawbacks, finding an efficient, time-saving preparation method of the bifunctional catalysts with high activity becomes an urgent topic.

Most researchers paid their attentions on the catalyst compositions, preparation conditions (such as pH, precipitation temperature, and calcinations temperature) and acid strength or distribution of the bifunctional catalyst for STD process [11,12]. However, it is very difficult to keep a good balance between CO conversion with high DME selectivity and the long life for hybrid catalysts only through this route.

More recently, Tsubaki et al. found that a series of zeolite capped Cu–ZnO catalysts which possessed a special core-shell structure could provide a tailor-made confined reaction environment and control the occurrence of the two reactions in a consecutive order that gave rise to an extreme selectivity for desired products compared with the conventional mechanically mixed hybrid catalysts [9,13]. These achievements indicated that the fine designed

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structure is more effective to catalytic performance than its own compositions.

In the present investigation, we want to report another special core-shell structured bifunctional catalyst (a H-ZSM-5 zeolite core enwrapped by one layer of a CuO-ZnO shell, denoted as CuO-ZnO@H-ZSM-5, abbreviated as CZ@H) for the STD process. These catalysts were prepared by means of simple homogeneous precipitation through urea hydrolysis. Characterizations disclose that these bifunctional catalysts possess high Cu surface area as well as high Cu dispersion, and consequently display an excellent catalytic performance.

2. Experimental

2.1. Catalyst preparation

First, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea were dissolved in 1.2 L deionized water in which the molar ratio of Cu/Zn was fixed to 2.2 (as shown in Fig. 1), and the required quantity of H-ZSM-5 (Si/Al = 22) was added under vigorous stirring. Then the resulting suspension was refluxed at 89 °C until the final pH reached 6.5–7.0. The precipitates were filtered, washed with deionized water and dried overnight at 80 °C followed by calcination at 350 °C for 4 h. The resulting catalyst was named as CZ@H(*x*), where the “*x*” stands for the weight ratio of CuO-ZnO/H-ZSM-5.

The CuO-ZnO catalyst was prepared by the same procedure but without adding H-ZSM-5, and named as CZ. Those bifunctional catalysts were also prepared by mechanical mixing of H-ZSM-5 with CZ (denoted as CZ/H(*x*)-M) and co-precipitation impregnation of CuO-ZnO on the surface of H-ZSM-5 (denoted as CZ/H(*x*)-C) as described in reference [5,14].

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-2500 diffractometer in a 2θ range of 5–80° (with a 2θ step of 0.02°) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). N_2 adsorption was carried out at –196 °C using an auto-adsorption analyzer (Micromeritics, TriStarII). Scanning electron images (SEM) and surface compositions of these core-shell catalysts were collected on JEOL (JSM6700F) and energy dispersive spectroscopy (EDS), analysis was carried out at an accelerating voltage of 15 kV. Temperature-

programmed reduction with H_2 (H_2 -TPR) of the calcined catalysts were carried out in a quartz reactor from 50 to 450 °C at a ramp of 10 °C/min in 10% H_2/N_2 (30 mL/min). The acidity of reduced catalysts were carried out via temperature-programmed desorption of NH_3 (NH_3 -TPD) from 100 to 550 °C at 10 °C/min. These procedures were addressed in Supplementary data in detail.

2.3. Catalytic reactions

CO hydrogenation experiments were carried out using a stainless steel tubular, high pressure, fixed-bed reactor (MCRS8400, China), which contained 0.5 g (20–40 mesh) catalyst placed between two layers of quartz (Fig. 2). Prior to catalytic experiments, all the catalysts were reduced by using a pure H_2 flow at 270 °C for 1 h under atmospheric pressure. Then, the reactor was cooled to 180 °C and the reactant gas flow was introduced, raising the pressure to 2.0 MPa and the temperature to a given temperature. The following reaction conditions were employed during activity test: $T = 220$ –280 °C; $P = 2.0$ MPa; gas hourly space velocity (GHSV) = 1500–7500 mL/(g_{cat} h), and the molar feed composition of $\text{H}_2/\text{CO} = 2$. All post-reactor lines and valves were heated to 150 °C to prevent product condensation. The flow rate (F_{total} , mL/min) of the vent gases was measured by a wet flow meter, and the composition (y_i) of effluent was analyzed by on-line with a gas chromatograph (HP5890, series II). And the conversion of CO was calculated as:

$$X_{\text{CO}} = \frac{y_{\text{CO}} F_{\text{total}} - F_{\text{CO-in}}}{F_{\text{CO-in}}} \times 100\% \quad (1)$$

The selectivity of DME, methanol and CO_2 was calculated in the following equations:

$$S_{\text{DME}} = \frac{2 \times y_{\text{DME}} \times F_{\text{total}}}{F_{\text{CO-in}} \times X_{\text{CO}}} \times 100\% \quad (2)$$

$$S_{\text{MeOH}} = \frac{y_{\text{MeOH}} \times F_{\text{total}}}{F_{\text{CO-in}} \times X_{\text{CO}}} \times 100\% \quad (3)$$

$$S_{\text{CO}_2} = \frac{y_{\text{CO}_2} \times F_{\text{total}}}{F_{\text{CO-in}} \times X_{\text{CO}}} \times 100\% \quad (4)$$

3. Results and discussions

3.1. Textural and structural properties

A series of core-shell structured CZ@H catalysts with controlled Cu/Zn = 2.2 and varied weight ratio between CuO-ZnO and H-ZSM-5 were prepared via urea hydrolysis at 89 °C. The XRD patterns of these core-shell catalysts are showed in Fig. 3. The typical diffraction peaks of H-ZSM-5 were observed in the 2θ ranges of 5–10° and 21–25° in all calcined catalysts, indicating that the structural integrity of H-ZSM-5 was well-preserved after this hydrothermal synthesis treatment. With the increasing CuO-ZnO/H-ZSM-5 ratio from 2.5 to 12.5, the diffraction lines of H-ZSM-5 became weaker and smaller, while led to a reverse variation for that of CuO and ZnO phases, suggesting that the presence of well shell structured and high crystallization degree of CuO species. The crystallite size of CuO increased from 10.9 nm to 15.6 nm with the increase of weight ratio (from 2.5 to 12.5), which was estimated from the diffraction peak at $2\theta = 38.8^\circ$ using the Scherrer's equation (summarized in Table 1). These results indicate that the homogeneous precipitation method through urea hydrolysis is capable of yielding nano-sized, well-dispersed core-shell structured catalyst.

Representative N_2 adsorption/desorption isotherms and pore-size distributions of CZ@H shell-core catalysts are provided in Fig. S1 (see the Supplementary data) that the surface area decreased

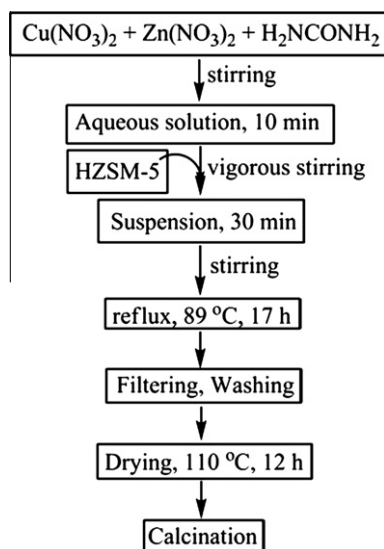


Fig. 1. Preparation procedures of the CZ@H bifunctional catalyst.

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