

Microstructure characters of Cu/ZnO catalyst precipitated inside microchannel reactor



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ABSTRACT

Cu/ZnO catalyst was prepared by co-precipitation method inside microchannel reactor and characterized by X-Ray diffraction (XRD), thermo gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM). The XRD analysis of precursors demonstrates that, compared with the sample prepared by conventional batch reactor, more Zn²⁺ are incorporated into malachite structure, which is attributed to the relatively uniform distribution of Cu, Zn elements in initial precipitates caused by the excellent mixing performance of the microchannel reactor. Higher decomposition temperature of carbonate species trapped in the interfaces between CuO and ZnO and higher binding energy of Cu2p_{3/2} indicate that sample prepared by the new reactor possess a stronger interface interaction, which derives from the more intimate contact between oxide components. This supposition is confirmed by the HRTEM images and the stronger interface interaction in the final reduced catalyst can improve catalytic performance on methanol synthesis.

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1. Introduction

The well-known Cu/ZnO/Al₂O₃ catalyst has been widely employed in methanol synthesis from syngas for more than 40 years [1]. The binary Cu/ZnO catalyst system with a Cu:Zn ratio of 7:3 serves as a model for investigating the characters of the industrially applied ternary catalysts [2]. The synthesis process is started by co-precipitation reaction between aqueous solutions of metal nitrates and sodium carbonate. During the following ageing process, the initial products are transformed into crystalline precursor and correspondingly Cu²⁺ in malachite are gradually substituted by Zn²⁺, forming the most active precursor, e.g. zincian malachite [3]. Active catalysts are obtained after the subsequent drying, calcination and reduction steps. The exposed Cu surface area and its intrinsic activity [4–6] are regarded as crucial factors with respect to the catalyst's performance. According to the previous literature [5], these two factors are deeply affected by the microstructure of final Cu/ZnO catalyst which is predetermined by the various synthesis parameters during the preparation process, and this phenomenon is termed as “chemical memory” of the system.

As well known, the precipitation process of Cu²⁺, Zn²⁺ has a close relationship with the preparation parameters and styles [7]. In the normal concentration range of reagents, the precipitation reaction is a very fast process which is more rapid than the mixing process of reagents, resulting that the precipitation process occurs under inhomogenous mixing conditions [8]. Combined with the fact that Cu, Zn cations have inconsistent precipitation conditions and rates, the distribution of Cu, Zn elements in initial precipitate is inevitably inhomogeneous. It seems the redissolution and recrystallization [9] processes in subsequent ageing step could smooth and even eliminate the inhomogeneity, however, the pronounced “chemical memory” phenomenon indicates the initial uneven character has been taken into the microstructure of final catalyst.

The conventional preparation of Cu/ZnO catalyst is carried out in the batch reactors, in which even under “constant” precipitating conditions the chemical potential of reagents are neither spatially nor temporally homogenous [10]. Thus, the inconsistency on mixing and reaction conditions at different time and position inevitably bring about the uneven distribution of Cu, Zn elements and effects on the final microstructure of catalysts. Accordingly, to some extent the Cu surface area and its intrinsic activity are influenced.

In the past years, microchannel reactors have aroused extensive attention. They are widely used in preparing nanoparticles and can be regarded as continuous and steady state flow devices in which the reaction conditions do not change with the time. Furthermore,

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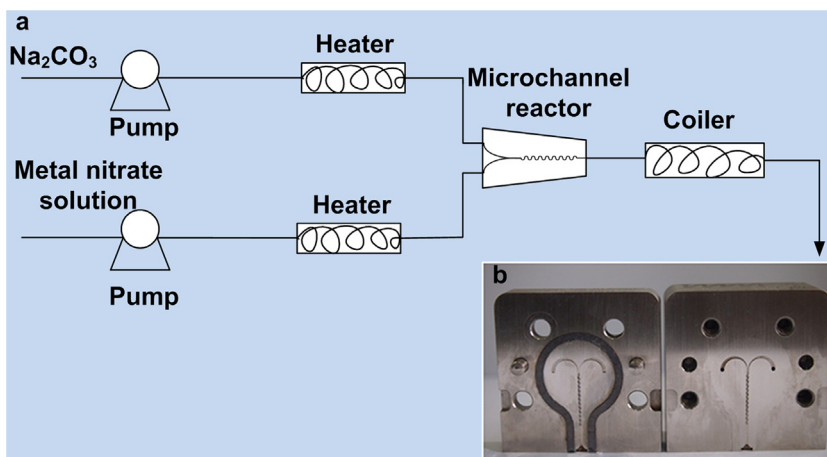


Fig. 1. (a) the scheme of preparation process by microchannel reactor (b) the photograph of inner flow channel of the microchannel reactor.

their tiny space and turbulence-inducing inner structure and configuration can significantly enhance and homogenize the mixing degree [11] in the channel. In this article we discuss the influences of these new features on the microstructure of precursors and catalysts.

2. Experiment methods

2.1. Catalyst preparation

The Cu, Zn (Cu/Zn molar ratio = 7/3) nitrate solution (0.4 M) and the aqueous Na_2CO_3 solution (0.4 M) were preheated to reaction temperature (70 °C), and then were simultaneously pumped into the microchannel reactor which has internal bas-relief structures to enhance the mixing degree of reagents (the scheme of preparation process and the image of inner flow channel of microchannel reactor are shown in Fig. 1). The mixed materials flowed through a coiled tube (20 m length, 2 mm ID) submerged in 70 °C water bath, and the pH value at outlet was regulated to set value by controlling the flow rate. After a 2 h ageing process, the obtained products were collected by filtration, and washed 6 times with deionized water. Subsequently, the samples were dried at 110 °C for 16 h followed by calcination at 350 °C in static air for 4 h. Finally the oxide components were reduced by 20 vol% H_2 in N_2 at 300 °C for 2 h.

For comparison, the conventional co-precipitation catalyst was prepared under the same conditions expect that precipitation process was conducted in a batch reactor with stir bar. Samples prepared by microchannel reactor and conventional batch reactor are respectively labeled as MR-X, BR-X, X represents for precursor, oxide, or catalyst.

2.2. Characterization method

X-ray powder diffraction (XRD) was performed on a X'Pert Pro MPD X-ray diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406$ nm). Thermogravimetric analyses were performed on a Netzsch STA449 thermobalance (10 K/min, synthetic air). XPS measurements were performed using a Physical Electronics PHI-5400 ESCA work station equipped with a magnesium anode ($\text{Mg K}\alpha = 1254$ eV) at a power of 240 W (12 kV and 20 mA). A Tecnai G2 F20 microscope operated at 200 kV and equipped with a field emission gun was used for HRTEM. Cu surface area was measured by applying N_2O reactive frontal chromatography (RFC) [12].

Table 1
the lattice plane reflection characters of two precursors.

	$\bar{1}20$ (2 θ)/°C	$\bar{1}21$ (2 θ)/°C	d (20 $\bar{1}$)/Å
BR-Precursor	32.15	33.15	2.761
MR-Precursor	32.40	33.29	2.744

2.3. Catalytic reaction

Catalysis activity measurement was performed in an up-flow tubular reactor (inner diameter 4 mm) made of stainless steel, loaded typically with 0.1 g of powder catalyst diluted with 1.0 g of quartz sand in 40–60 mesh. The reduced catalyst was maintained at 220 °C for 2 h in N_2 flowing at 40 ml/min. Then, syngas (H_2 : $\text{CO} = 2:1$, with Ar as the internal standard, the specific proportions respectively are 64.2%, 32.1% and 3.7%) with a total flow rate at 60 ml/min (GHSV = 10276 h^{-1}) was switched in. The catalytic activity was determined under the following conditions: pressure 2 MPa, temperature range 220 °C–270 °C. After leaving the reactor, the organic products were analyzed by on-line GC (model 1102) equipped with a FID detector and the inorganic products were analyzed by on-line GC (model 9790) equipped with a TCD detector. The CO conversion was calculated from the formula: $X(\text{CO}) = (\text{Mol}(\text{CO})_{\text{in}}/\text{min} - \text{Mol}(\text{CO})_{\text{out}}/\text{min})/\text{Mol}(\text{CO})_{\text{in}} \times 100\%$, $\text{Mol}(\text{CO})_{\text{in}}/\text{min}$ and $\text{Mol}(\text{CO})_{\text{out}}/\text{min}$ were respectively denoted the molar flow-rate of CO in inlet and outlet. Methanol production on per unit copper surface area was used to evaluate the catalytic performance.

3. Results and discussion

3.1. Microstructure characterization of precursors

The XRD patterns of the precursors prepared by two methods were shown in Fig. 2. All the marked peaks belong to the reflections of zincian malachite (JCPDS-PDF 41-1390). As shown in the figure, the reflections of 20 $\bar{1}$, 21 $\bar{1}$ lattice planes of zincian malachite in the MR-Precursor shift towards higher angles and the corresponding d-spacing of 20 $\bar{1}$ reflection has a lower value (see Table 1). Pointed in the literatures, the observed phenomenon is indicative of more Cu^{2+} (d^9 , Jahn-Teller distorted coordination preferred) substituted by Zn^{2+} [d^{10} , no Jahn-Teller distortion], which would exert a larger contraction on the Jahn-Teller distortions of MO_6 octahedral in the malachite structure and thus lower the d-spacing value of 20 $\bar{1}$ reflection. Estimated by the established function [9] between the amount of incorporated Zn^{2+} and d-spacing value, the Zn content in

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