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Microwave-assisted synthesis of high performance copper-based catalysts for hydrogen production from methanol decomposition

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ABSTRACT

High performance copper-based catalysts (CuNiZnO/ γ -Al₂O₃) for hydrogen production from methanol decomposition were successfully synthesized by the method of microwave-assisted thermal hydrolysis of urea. The ICP-OES, N₂ adsorption–desorption, SEM, TEM, XRD and H₂-TPR were applied to characterize the physicochemical properties of the prepared materials. These experiment results reveal that the higher thermal treatment temperature can improve the catalytic performance by enlarging the content of promoters (Zn and Ni) and promoting the dispersion of deposited particles. Moreover, the addition of Ni can significantly improve the catalytic performance of the copper-based catalysts, which is ascribed to the regulation of reaction process and inhibition of Cu–Zn alloy. Among the obtained catalysts, the MW-Cu/Ni-95 developed at 95 °C exhibits a higher catalytic activity, which reaches 91.7% conversion at 250 °C. Most significantly, it shows the excellent catalytic performance as compared with the commercial catalyst under the same test conditions.

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Introduction

Combustion of fossil fuels has aroused widespread citizen concerns for energy and environment issues that are critical for human life, which has stimulated research into new and clean sources [1–4]. Hydrogen has been considered as a clean and renewable energy [5–9], owing to the fact that its ultimate burning product is only H₂O without any pollutants and greenhouse gases [10,11], which play a significant role in preventing the further deterioration of global ecological environment. However, the transportation of hydrogen

usually needs to be carried out under high pressure [12,13], which fades its large-scale industrial applications. Fortunately, this problem can be solved by using the steam reforming of natural gas, coal and other fossil fuels to produce the hydrogen in situ [14–16]. Nevertheless, these technologies will consume a lot of fossil fuels, which could accelerate the energy crisis. What's worse, the exhausted gases such as CO₂, SO₂ and NO_x [14], would exacerbate the greenhouse effects and environment pollution. Therefore, it is very significant to find a clean and sustainable alternative material to produce hydrogen in situ.

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Methanol, as a common chemical raw material, has a simple molecular structure, high hydrocarbon ratio and low reforming temperature [17–20]. Most significantly, it can be produced by sustainable biomass and its reserve and transportation are also simple and safe [12]. Therefore, the methanol has been regarded as a promising alternative to fossil fuels for the hydrogen production [12]. There are four technological routes for the preparation of hydrogen from methanol: methanol decomposition ($\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$), methanol oxidation ($\text{CH}_3\text{OH} + 1/2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2$), methanol steam reforming ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$) and methanol oxidative steam reforming ($\text{CH}_3\text{OH} + (1-n)\text{H}_2\text{O} + 1/2n\text{O}_2 \rightarrow \text{CO}_2 + (3-n)\text{H}_2$) [9,15,21]. Particularly, methanol decomposition realized at lower temperature exhibits an operational convenience and economic advantage among them [22]. Thus, it has been used in small-scale production of hydrogen and the recovery of the waste heat from industries and automobiles [22,23]. The catalysts for methanol decomposition include noble metal catalysts such as Pt, Pd [24,25] and transition metal catalysts like Cu, Fe [26,27]. Among these catalysts, the copper-based catalysts have been attracted extensive research interest due to the fact that the Cu is cheap and exhibit excellent catalytic activity at lower reaction temperature [25,28–32]. However, the catalytic performance of these reported copper-based catalysts for methanol decomposition can be further enhanced by improving the dispersion of active phase and adding promoters.

Recently, the microwave heating technology, an efficient saving-energy technique, that use the electromagnetic wave and electromagnetism field to heat the things [33], has been widely used in the synthesis of organic and inorganic chemistry [34–36]. Compared with the heat transfer of the traditional heating technology, which is important phenomenon in many processes [37], that of microwave heating is non-contact between heating source and heating substances. Moreover, microwave heating has the following advantages [33,34,38]: (i) rapid heating; (ii) easy control of the reaction conditions; (iii) uniform heating for the substances with same microwave absorbing properties; (iv) selective heating for the substances with different microwave absorbing properties; (v) higher yields. Therefore, the microwave heating technology is able to obtain more uniform nucleation and small nanoparticles (diameter of about 1–100 nm) with less energy consumption [39–42].

In this work, the method of microwave-assisted thermal hydrolysis of urea was applied to fabricate the copper-based catalysts for hydrogen production from methanol decomposition and the effects of microwave heating temperature and promoter on the catalytic performance of the prepared materials were systematically discussed.

Experimental

Catalyst preparation

Pretreatment of catalyst support. The spherical gamma alumina was shredded to obtain 20–40 mesh particles. Then the obtained particles were washed three times with deionized water and anhydrous ethanol, respectively, and dried at

100 °C overnight. After dried, these particles were placed into the muffle furnace and activated at 500 °C for 4 h. Finally, the $\gamma\text{-Al}_2\text{O}_3$ powder was obtained by grinding these activated gamma alumina particles.

Preparation of $\text{Cu}^{2+}/\text{Zn}^{2+}$ mixture solution. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and deionized water were used to prepare the $\text{Cu}^{2+}/\text{Zn}^{2+}$ mixture solution. The concentration of Cu^{2+} and Zn^{2+} was 1 mol/L, respectively.

Synthesis of the catalysts: 10 ml $\text{Cu}^{2+}/\text{Zn}^{2+}$ mixture solution, 40 ml deionized water, 0.001 mol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.42 mol urea and 0.006 mol $\gamma\text{-Al}_2\text{O}_3$ powder support were added to a 250 ml three-necked flask and were stirred vigorously. Next, the flask was placed in an ultrasound device and sonicated for 0.5 h at a power output of 100 W. Then, the flask was put into the microwave oven (XH-MC-1, Xianghu Co., Beijing) to be heated. The heating temperature was 80 °C (85 °C, 90 °C or 95 °C) at a power output of 500 W for 2.0 h. Next, the suspension was poured into a 500 ml beaker and aged at 35 °C for 20 h. After that, the suspension was filtered, washed three times with deionized water and then dried at 100 °C for 20 h. Afterwards, the precursor was calcined at 350 °C for 5 h in static air. Finally, the sample was compressed and then shredded to obtain 20–40 mesh particles. The four samples were denoted as MW-Cu/Ni-80, MW-Cu/Ni-85, MW-Cu/Ni-90 and MW-Cu/Ni-95, respectively. Sample MW-Cu-95 was prepared following the same procedure of the sample MW-Cu/Ni-95 without the addition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The commercial catalyst (CM) for methanol decomposition, purchased from Alibaba (Lanzhou zhongke kaidi chemical new technology Co., LTD, China), was shredded to obtain 20–40 mesh particles.

Catalyst characterization

The inductively coupled plasma optical emission spectrometer (ICP-OES) was conducted on Agilent (Germany) to determine the element contents of samples.

The N_2 adsorption–desorption isotherms were measured at 77 K on an automated surface area & pore size analyzer (NOVA 1000e apparatus, Quantachrome). Before measurement, all the samples were degassed at 200 °C for 3 h. The specific surface areas were calculated using the equation of Brunauer-Emmett-Teller (BET) and the pore size distribution was obtained from desorption branch of isotherms by using the Barrett-Joyner-Halenda (BJH) method.

The scanning electron microscope (SEM) was recorded on Zeiss ultra55 at 15 KV and the analysis of transmission electron microscope (TEM) for the samples reduced in the mixture gas (H_2/Ar) was obtained using JEOL JEM-2100F at 200 KV.

The X-ray diffraction (XRD) patterns of the catalysts reduced in the mixture gas (H_2/Ar) were performed on the DX-2700 diffractometer (Haoyuan, China) using $\text{Cu K}\alpha$ (40 kV, 30 mA) radiation ($\lambda = 0.15418$ nm) in the scanning angle (2θ) range of 5°–80° with a scanning rate of 0.03°/s.

The H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) measurement was carried out in a fixed-bed reactor under atmospheric pressure using SC-200 gas chromatography with a thermal conductivity detector (TCD) for on-line analysis. 10 mg catalyst was placed in the middle of quartz reactor tube and the gas flow rate of reduction gas with 5% H_2/N_2 was 30 mL/min. The temperature of the reactor was firstly raised

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