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# A facile and rapid route to synthesize $\text{CuO}_x/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ catalysts with high performance for CO preferential oxidation (CO-PROX)

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## ABSTRACT

$\text{CuO}_{(10)}-\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2\text{-UGC-300}$  ( $\text{CuO}-\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  prepared by urea grind combustion method, with 10 wt.% CuO loading and calcined at 300 °C) and  $\text{CuO}_{(10)}-\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2\text{-IWI-300}$  (prepared by incipient wetness impregnation method) catalysts were tested for CO-PROX. It was noticed that both the CO conversion and the  $\text{O}_2$  selectivity of  $\text{CuO}_{(10)}-\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2\text{-UGC-300}$  are higher than those of  $\text{CuO}_{(10)}-\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2\text{-IWI-300}$ . The high performance catalytic activities of  $\text{CuO}_{(10)}-\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2\text{-UGC-300}$  have been attributed to the synergistic effects of highly dispersed Cu species together with the stronger interaction between CuO and the support. The effect of the CuO content and calcination temperature on the catalytic activity of the  $\text{CuO}-\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  catalysts were investigated in detail. The catalyst with 10 wt.% CuO loading and calcined at 300 °C exhibited the highest catalytic activity.  $\text{CuO}_{(10)}-\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2\text{-UGC-300}$  catalyst exhibited excellent adaptability of space velocity from 12,000  $\text{h}^{-1}$  to 36,000  $\text{h}^{-1}$  and with good tolerance towards  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

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## Introduction

Proton exchange membrane fuel cells (PEMFCs) have recently garnered much research attention for both mobile and stationary energy applications due to its high energy and power densities. The PEMFC currently requires hydrogen as its fuel source. Hydrogen fuel is usually produced by steam reforming of hydrocarbons or alcohols followed by the WGS reaction [1].

However, a CO concentration of about 1% is obtained from those reaction processes, which, unfortunately, is much higher than the 10 ppm level desired for practical fuel cell applications [2–4]. The CO concentration in the cell feed needs to be as low as 20 ppm to prevent poisoning the platinum anode [5–8]. CO preferential oxidation (CO-PROX) is currently used for the purification of these CO-contaminated  $\text{H}_2$ -rich streams due to its efficiency and simplicity, which allows for

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small scale operation for portable applications. Catalysts reported to be active for CO-PROX reaction are classified into two types, namely noble metal catalysts and non-noble metal catalysts. Among them, noble metal catalysts are the most effective for CO oxidation. However, exorbitant price and scarce resource discourage their extensive applications. Recently, Cu–Ce based catalysts have been proposed as a candidate for the selective oxidation of CO in the presence of excess hydrogen [9–14].

So far, mixed oxide containing CeO<sub>2</sub> and ZrO<sub>2</sub> was studied by many researchers [15–17]. It has been reported that the role of Zr is to control the structure or the sites of cerium oxide crystallite [18]. This was found to be due to the formation of Ce–Zr solid solution, which leads to promotions in oxygen storage capacity, redox property, thermal resistance of the resulting mixed oxide [18–23] and better catalytic performance for CO oxidation [24] and combustion of methane [25]. Chen et al. [26] systematically investigated the impact of Ce/Zr ratio on the CuO/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> materials, and concluded that an appropriate amount of Zr added to CeO<sub>2</sub> would increase the mobility of lattice oxygen and promote the activity of the CO preferential oxidation. Of late, researchers have developed various synthesis methods to improve catalytic behaviors of CuO<sub>x</sub>–Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> for CO-PROX [27–29]. The preparation method of catalyst is one of key parameters needed to be optimized, which would result in different structural and textural properties of Cu-based catalyst. Cao et al. [27] prepared Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support by three different methods (surfactant-assisted, co-precipitation, and sol–gel), and CuO was supported on Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> by deposition-precipitation method. They found that the catalyst prepared by surfactant-assisted method was more active for CO oxidation than the other two catalysts. And it possessed mesoporous framework, high surface area and nanoscale particle size, improving the synergistic effect between CuO species and Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>, which is in favor of enhancing the catalytic performance of CO oxidation. Although those preparation methods are beneficial to catalytic activity of catalysts, the procedures of preparation are complex and time-consuming. Therefore, searching out a method to simplify producing processes and shorten preparation time is practically significant for the preparation of catalysts.

In this work, we reported a facile and rapid route (urea grind combustion (UGC) method) to synthesize high performance CuO–Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalyst (CuO–Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>-UGC) within 20 min and compared the catalyst to CuO–Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>-IWI (prepared by incipient wetness impregnation method) for CO-PROX. Then, the effects of synthetic parameters (copper loading and calcination temperature) on catalytic performances of CuO–Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>-UGC were investigated. Finally, the influence of space velocity on the catalytic performances and the stability of the catalyst were studied.

## Materials and methods

### Catalyst preparation

CuO<sub>x</sub>–Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>-UGC-T catalysts synthesized by urea grind combustion (UGC) method were briefly described as follows:

Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O and (NH<sub>2</sub>)<sub>2</sub>CO were mixed and grinded in agate mortar under room temperature until the transparent viscous gel was obtained. After that, the gel was calcined at 300 °C for 15–20 min. In order to investigate the effect of calcination temperature, the gel was calcined at 400 °C and 500 °C, respectively. All the catalysts synthesized via this route were denoted as CuO<sub>(x)</sub>–Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>-UGC-T, where “x” and “T” represent the CuO loading (5–20 wt.%) and calcination temperature (300–500 °C), respectively.

For comparison, a sample was prepared by incipient wetness impregnating Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> with aqueous Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O solution. Then, the sample was kept at the room temperature for 12 h. Subsequently, the sample was dried at 120 °C for 8 h and calcined at 300 °C for 2 h. The catalyst was denoted as CuO<sub>(10)</sub>–Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>-IWI-300.

### Catalyst characterization

X-ray diffraction (XRD) patterns were performed on the Rigaku D/max-1200 diffractometer by using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at  $2\theta$  range between 10 and 90°. High-resolution transmission electron microscopy (HRTEM) images of the samples were obtained using the JEOL JEM-2100 microscope with an accelerating voltage of 200 kV. H<sub>2</sub> Temperature programmed reduction (H<sub>2</sub>-TPR) were performed in a quartz tube reactor. Prior to the TPR experiment, 50 mg of sample were pretreated at 400 °C under 5 vol.% O<sub>2</sub>/Ar mixture gas for 1 h, then cooled to 100 °C in the flow of ultra-pure argon gas. After that, TPR experiments were carried out in 10% H<sub>2</sub>/Ar (30 cm<sup>3</sup>/min) increasing the temperature from 50 °C to 900 °C with a heating ramp of 10 °C/min. Hydrogen consumption was detected by on-line TCD detector. The surface element compositions and the corresponding chemical states of the sample were determined by X-ray photoelectron spectroscopy (XPS) performed on a PHI 5000 VersaProbe II with non-monochromatic Al K $\alpha$  radiation (1486.6 eV) as the excitation X-ray source.

### Catalytic activity measurement

CO selective oxidation in hydrogen-rich gas was carried out in a tubular reactor under atmospheric pressure. 150 mg catalyst was diluted with quartz sands (both in 40–60 mesh) and loaded in quartz tubular reactor. A K-type thermocouple was inserted into the catalyst bed to monitor the reaction temperature. The composition of typical feed gas mixture was 1% CO, 1% O<sub>2</sub>, 50% H<sub>2</sub> in volume and with He as balance gas, and the total gas flow rate was 80 ml/min, corresponding to the gas hourly space velocity (GHSV) of 24,000 h<sup>-1</sup>. The exit gases from the reactor were analyzed by on-line gas chromatography with a thermal conductivity detector (TCD), a flame ionization detector (FID) together with a methanation reactor. The catalytic activities were expressed in terms of CO conversion (%) and O<sub>2</sub> (%) selectivity, which were calculated based on the CO consumption, as shown below:

$$\text{CO conversion}(\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (1)$$

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