

High potential of mesoporous ceria/ceria-zirconia synthesized via nanocasting pathway for catalytic applications

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ABSTRACT

Presently, nanocasting process, an alternative synthesis pathway, has been widely employed to synthesize ordered nonsiliceous mesoporous materials. In this work, mesoporous CeO₂ (C) and mesoporous CeO₂-ZrO₂ (CZ), were successfully prepared via nanocasting method using MCM-48 as a hard template. Both C and CZ supports provided ordered structure with high specific surface area. Copper (Cu) loaded onto C and CZ supports by deposition-precipitation (DP) method exhibited high dispersion of Cu species. The structures and properties of both catalysts play a crucial role to interesting catalytic applications, such as preferential oxidation of CO (CO-PROX) and oxidative steam reforming of methanol (OSRM). The Cu-C and Cu-CZ catalysts showed good potential for CO-PROX reaction with 100% CO conversion at 110° and 130 °C, respectively, and also exhibited excellent catalytic performance for OSRM reaction with 100% methanol conversion at 350° and 300 °C, respectively.

Keywords: Mesoporous ceria/ ceria- zirconia, Catalytic applications

1 INTRODUCTION

Porous materials, divided into three classes; microporous (<2 nm), mesoporous (2-50 nm) and macroporous (>50 nm) materials [1], have been extensively studied for several applications, especially ordered mesoporous materials. Due to their extremely large surface area within a relatively small volume, mesoporous materials show promising potential to use as adsorbents, catalysts, catalyst supports, chemical sensors and molecular separation [2,3]. An alternative synthesis pathway, nanocasting process, has been developed to obtain ordered nonsiliceous mesoporous materials that are difficult to synthesize by conventional processes [4]. The nanocasting process involves in three main steps: i) formation of the template; ii) the casting step with precursors and iii) removal of the template [5]. This method can occur in a limited nanospace of template and the sintering of precursors is restricted in the limited nanopores, resulting in the achieved materials having high surface area and special nanostructure [6]. The hard templates for nanocasting process show important potential over the soft template because the hard templates provide well-ordered structure of frameworks,

generating high surface areas and ordered structure of replica [7]. Cubic MCM-48 as mesoporous material, indexed in the space group of *Ia3d*, is a good candidate using as hard template in nanocasting process on account of its three-dimensional pore structure and interconnected channels, reducing diffusion limitations and avoiding pore blockage of reactants [8].

Ceria (CeO₂, C), a fluorite-type oxide, is the most important rare-earth oxide for the oxidation reactions because of its redox cycle between Ce⁴⁺ and Ce³⁺ and high oxygen storage capacity (OSC) [9,10]. Furthermore, the introduction of zirconia (ZrO₂, Z) to C is an alternative way to improve thermal resistance, redox property, and oxygen storage and release capacity of pure C [11]. Therefore, both C and CZ are the excellent supports for many metal catalysts. In this study, mesoporous C and mesoporous CZ supports were prepared via nanocasting process using MCM-48 as hard template. Cu catalyst was loaded onto supports by the deposition-precipitation (DP) method. The catalytic performance of Cu loaded onto the mesoporous C and CZ supports (Cu-C and Cu-CZ) was evaluated by preferential oxidation of CO (CO-PROX) and oxidative steam reforming of methanol (OSRM).

2 EXPERIMENTAL

2.1 Preparation of mesoporous CeO₂ and CeO₂-ZrO₂

Mesoporous C and CZ supports were prepared via nanocasting process using MCM-48 as hard template. In case of mesoporous C preparation, 50 wt% of Ce(NO₃)₃·6H₂O as a precursor and 50 wt% of MCM-48 were mixed in 5 ml of ethanol and continuously stirred for 30 min. For preparation of mesoporous CZ, Ce(NO₃)₃·6H₂O and ZrOCl₂·8H₂O in a molar ratio of Ce:Zr = 0.75:0.25 were dissolved in 5 ml of ethanol and then MCM-48 was directly added to the mixture, with constant stirring for 4 h. Then, ethanol was removed by evaporation in an oven at 100 °C. The dried powder was calcined at 550 °C for 6 h. MCM-48 was removed by 2 M NaOH at 50 °C. The obtained product was washed with deionized water until neutral and dried overnight.

2.2 Preparation of Cu loaded mesoporous CeO₂ and CeO₂-ZrO₂

Cu loaded mesoporous C and CZ were synthesized by the deposition-precipitation (DP) method. Mesoporous C and CZ were added to aqueous solution of Cu(NO₃)₂·3H₂O and continuously stirred for 1 h at room temperature. Subsequently, the mixture was heated to 80 °C, and its pH adjusted to 7 by Na₂CO₃ before aging for another hour. The obtained product was filtered, washed with warm distilled water, dried overnight, and eventually calcined in air at 500 °C for 6 h.

2.3 Catalytic activity measurement

The synthesized catalysts were evaluated for the preferential oxidation of CO by packing 100 mg of catalyst into a U-tube between layers of glass wool. The reactant gas composition containing 1 vol.% CO, 1 vol.% O₂ and 40 vol.% H₂ balancing with He was fed into the CO-PROX reactor. The total flow rate of the mixed gas was about 50 ml min⁻¹. The effluent gas stream was detected by an on-line gas chromatograph (Agilent Technologies 6890N) using a carbosphere column and a thermal conductivity detector (TCD).

The prepared catalysts were also evaluated for oxidative steam reforming of methanol. A 100 mg of catalyst was packed in the reactor and fixed by two layers of quartz wool. The mixture of methanol and distilled water was continuously pumped by a syringe pump to a vaporizer in order to generate a vapor mixture of methanol and steam. The mixture vapor was mixed with He carrier gas (45 ml/min) and oxygen (5 ml/min) before being fed into the catalytic reactor. The product gas stream from the reactor were analyzed by a Hewlett Packard 5890 series II gas chromatograph equipped with a thermal conductivity detector (TCD) and carbosphere column.

3 RESULTS AND DISCUSSION

3.1 Characterization of synthesized catalysts

The mesoporous C and mesoporous CZ supports, preparing via nanocasting process using MCM-48 as template, show similar characteristic peaks at {211} and {220} to MCM-48. This result indicates that both mesoporous C and mesoporous CZ supports still maintain some order from the MCM-48 template.

The BET specific surface areas (S_{BET}) and the average mesopore diameter (d_{pore}) of mesoporous C and mesoporous CZ supports as well as Cu loaded mesoporous supports are summarized in Table 1. The prepared supports obviously show the high specific surface area with average pore diameters in the mesoporous range (2-50 nm) [1]. The addition of Cu onto supports causes the decrease of specific surface area of the catalysts because CuO can block the pores of supports and obstruct the N₂ adsorption in the BET experiment.

Table 1: N₂ physisorption data of the synthesized catalysts.

Sample	Sample acronym	Specific surface area (m ² g ⁻¹)	Mesopore diameter (nm)
CeO ₂	C	259	4.30
Cu-CeO ₂	Cu-C	206	4.63
CeO ₂ -ZrO ₂	CZ	256	3.80
Cu-CeO ₂ -ZrO ₂	Cu-CZ	165	3.61

The phase structure and crystallinity of both supports and Cu loaded mesoporous supports were confirmed by WAXD in a 2θ range of 20° and 80°, as shown in Figure 1. The main peaks of all samples appear at 28.71°, 33.31°, 47.96°, 56.95°, 59.24°, 70.00° and 76.93° corresponding to {1 1 1}, {2 0 0}, {2 2 0}, {3 1 1}, {2 2 2}, {4 0 0}, and {3 3 1} reflections, respectively, and representing the fluorite cubic structure [12,13]. Surprisingly, the addition of Cu into both C and CZ supports disappears the change of diffraction patterns and the intensity of peaks. Furthermore, there are no diffraction peaks of CuO phases at 2θ = 35.6° and 38.8°. It can be mentioned that the DP method provides the high dispersion of Cu on C and CZ supports. The absence of the CuO diffraction peak can also confirm that CuO crystallites are very small [9].

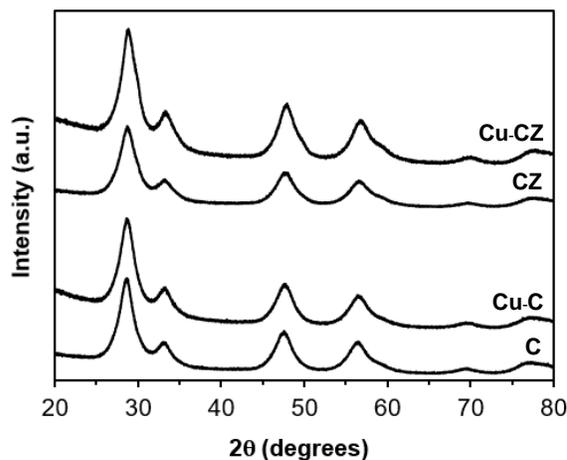


Figure 1: Wide angle XRD patterns of mesoporous C, mesoporous CZ, Cu-C, and Cu-CZ.

3.2 Catalytic activity for preferential oxidation of CO (CO-PROX)

The catalytic performance of Cu-C and Cu-CZ catalysts was investigated for CO-PROX reaction under an excess H₂ component in the temperature range of 50°–250 °C, as shown in Figure 2. At the first range of reaction temperature, CO conversion of both catalysts increase with increasing temperature, but the oxygen selectivity towards CO₂ decreases with temperature. Then, the Cu-C catalyst achieve 100% conversion at 110 °C while the Cu-CZ catalyst reached 100% conversion at 130 °C with the selectivity higher than 50%.

Generally, CuO acts as catalyst which can adsorb CO molecules and it is reduced by CO to produce CO₂ molecules. CeO₂ and CeO₂-based supports provides lattice oxygens for converting CO to CO₂ molecules. Oxygen competes with CO molecules in order to adsorb on the catalyst and oxygen vacancies are located at the Cu-CeO₂ interface [14]. Finally, oxygen can re-oxidize the surface metal atoms and repopulate oxygen vacancies on the C and CZ support [15]. The high activity and selectivity are the important evidence, indicating that the synthesized catalysts, ordered mesoporous material with high surface area, show good performance for CO-PROX reaction.

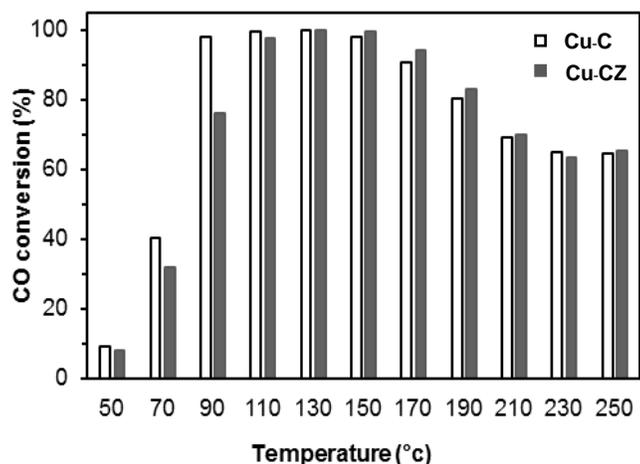


Figure 2: CO conversion as a function of temperature of Cu-C and Cu-CZ catalysts.

3. 3 Catalytic activity for oxidative steam reforming of methanol (OSRM)

The catalytic activity of Cu-C and Cu-CZ catalysts was evaluated for oxidative steam reforming of methanol in a temperature range from 200° to 400 °C, as illustrated in Figure 3. The Cu-C catalyst exhibits high methanol conversion more than 80% at the beginning of reaction temperature while the Cu-CZ catalyst achieves more than 90% methanol conversion at 200 °C. This result shows that the OSRM reaction is favored by increase of the reaction temperature. The Cu-C catalyst shows methanol conversion of 100% at 350 °C while the Cu-CZ catalyst achieve complete methanol conversion at 350 °C. The % H₂ yield of both catalysts corresponds to methanol conversion in a temperature range from 200° to 400 °C, providing a maximum % H₂ yield of 60%. Furthermore, CO production from OSRM reaction over Cu- C and Cu- CZ catalysts is quite low and H₂ and CO₂ are the primary products. Furthermore, it is found that CO formation increases with increasing temperature since CO molecules are generated at high temperature by the reverse water-gas shift reaction [16].

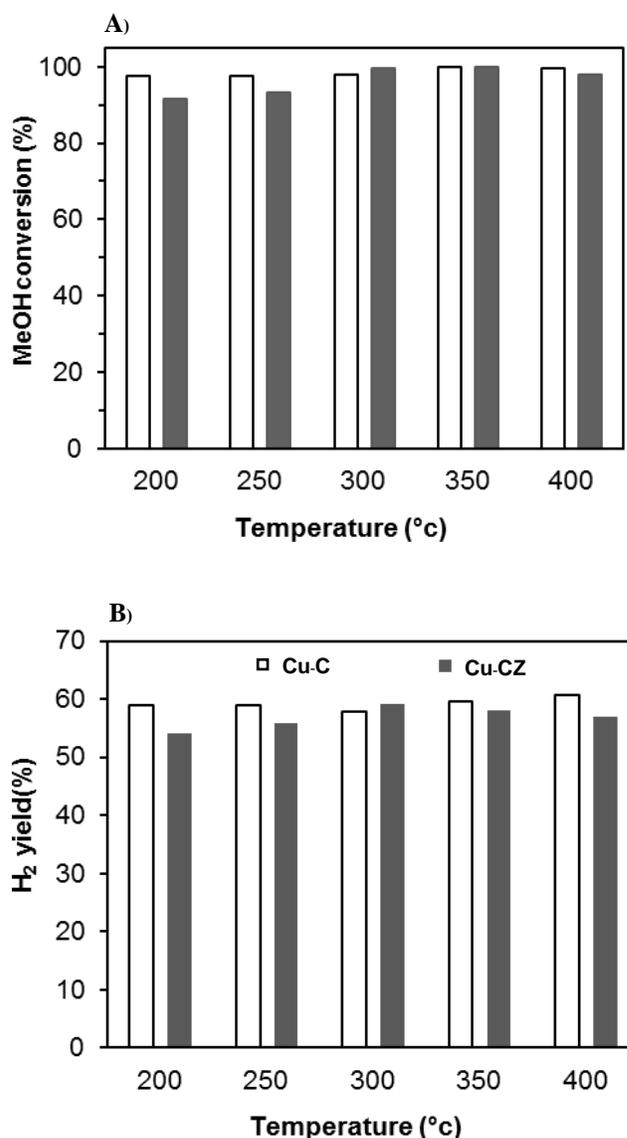


Figure 3: A) Methanol conversion and B) H₂ yield of Cu-C and Cu-CZ catalysts.

4 CONCLUSIONS

In this study, mesoporous CeO₂ and mesoporous CeO₂-ZrO₂ supports were successfully prepared via nanocasting process using MCM-48 as hard template. The C and CZ supports show an ordered mesoporous structure and a high surface area around 259 and 256 m²g⁻¹. The deposition-precipitation technique was used to load Cu onto C and CZ supports. Wide angle XRD spectra can confirm that the loading of Cu onto C and CZ supports does not the change of diffraction patterns and the peak intensity of supports. Moreover, there are no diffraction peaks of CuO phases, indicating that DP method provides the high dispersion of Cu on C and CZ supports. The Cu-C and Cu-CZ catalysts exhibit excellent performance for CO-PROX reaction. The complete CO conversion of Cu-C and Cu-CZ catalysts appears at the

reaction temperature of 110° and 130 °C, respectively. Furthermore, the OSRM results illustrate that Cu-C and Cu-CZ catalysts provide the best catalytic performance with 100% methanol conversion and 60% H₂ yield at 350° and 300 °C, respectively.

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