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Full Length Article

# Change of $Cu^+$ species and synergistic effect of copper and cerium during reduction-oxidation treatment for preferential CO oxidation

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ABSTRACT

The CuO-$CeO_2$@$SiO_2$ catalyst with flower-sphere morphology was prepared by the impregnation method and then experienced the reduction-oxidation treatment at different temperatures. The multi-technique characterization shows that the reduction-oxidation treatment can remodel CuO, improve textural and surface properties and change $Cu^+$ content and synergistic effect of copper and cerium. The importance of this work lies in the fact that the decrease of $Cu^+$ content and synergistic effect of copper and cerium that occurs in the reduction-oxidation process results in the decrease of catalytic activity over the CuO-$CeO_2$@$SiO_2$ catalyst for preferential CO oxidation. The process of reaction in rich-hydrogen streams is equivalent to a reduction procedure which decreases $Cu^+$ content and synergistic effect of copper and cerium.



## 1. Introduction

Many researches have focused on producing and delivering of clean hydrogen as the interest in proton-exchange membrane fuel cells (PEMFCs) increases [1–3]. Hydrogen for PEMFCs is usually generated by a multistage process including catalytic reforming of hydrocarbons and water-gas shift reaction. The resulting rich-hydrogen streams contain 0.5–2.0 vol% CO, which poisons Pt anode and must be removed to a trace level below 100 ppm [4–6]. Preferential oxidation of CO (CO-PROX) has been recognized as the most simple and cost-effective method to reduce CO from rich-hydrogen streams [4,7,8].

CuO-$CeO_2$ bimetal oxides are alternative catalysts to noble metals due to low cost and high catalytic performance in PROX reaction [9–16]. Catalytic performance is related to synergistic interaction of CuO-$CeO_2$ interfacial sites since activity of CO oxidation has been attributed to redox cycles of $Ce^{4+}/Ce^{3+}$ and $Cu^{2+}/Cu^+$, which are abundant in contact interface of copper and cerium [8,9,17–20]. The interfacial CuO is easily reduced to form $Cu^+$ species that is generally considered as CO adsorption sites. Meanwhile, oxygen vacancies at contact interface can capture gas-phase oxygen molecules which are driven into active oxygen species. CO molecules adsorbed onto $Cu^+$ would be quickly oxidized by adjacent active oxygen species [12,20]. Oxygen vacancies are reactivated and continuously capture gas-phase oxygen molecules to produce new active species around interface after desorbing oxygen [21,22]. However, CuO/$CeO_2$ catalyst usually decreases catalytic activity above 150 °C, which restricts the application of CuO/$CeO_2$ catalyst [23]. To solve this problem, the inverse $CeO_2$/CuO catalyst is developed since 2010 [12,14,23]. The inverse $CeO_2$/CuO catalyst will experience the decrease of catalytic activity above 180 °C although it has better high-temperature activity than the CuO/$CeO_2$ catalyst. Therefore, it is essential to explore the cause of the decrease of catalytic activity in hydrogen-rich streams.

The process of reaction in rich-hydrogen streams for CO-PROX is equivalent to a reduction procedure. It is reported that reshaping CuO on silica generates highly active Cu/$SiO_2$ catalyst via a reduction-oxidation treatment [24]. There is a memory effect of the shape of CuO to metal copper on silica during the reduction process [24]. Therefore, we hope to acquire the information about the change of copper species or synergistic interaction of copper and cerium by the reduction-oxidation treatment.

In this work, the $CeO_2$@$SiO_2$ support with flower-sphere morphology was prepared by the hydrothermal method, and the thin $SiO_2$ layer was incompletely coated on the surface in order to ensure contact between CuO and $CeO_2$. The CuO-$CeO_2$@$SiO_2$ catalyst was prepared by the impregnation method and then experienced reduction-oxidation treatment at different temperatures aiming to remodel CuO on silica. The multi-technique characterization was employed to correlate change of properties with catalytic

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performance. The goal is to gain a further insight into the essential of the decrease of catalytic activity during CO-PROX reaction.

## 2. Experimental

### 2.1. Catalyst preparation

The $CeO_2$@$SiO_2$ support with flower-sphere morphology was prepared by the two-step hydrothermal method [25]. The $C_6H_{12}O_6{\cdot}H_2O$ was dissolved in 60 mL distilled water. The solution was stirred vigorously and sealed into the Teflon-lined autoclave, and then the solution was heated at 180 °C for 4 h. After cooling to room temperature, the $Ce(C_2H_3O_2)_3{\cdot}1.5H_2O$ were added in the above solution and kept at 180 °C for 12 h. The obtained solid was washed and dried overnight at 80 °C. It was denoted as $CeO_2$@C.

The absolute ethyl alcohol, $NH_3{\cdot}H_2O$ and CTAB were added into a three-necked flask containing the $CeO_2$@C aqueous solution, respectively. The mixture was stirred and treated by ultrasonic wave for 30 min. Then, the TEOS was added dropwise into the mixture and stirred for 8 h. The mixture was washed by distilled water and absolute ethanol and dried overnight at 80 °C. Further, the solid was heated with a heating rate of 2 °C $min^{-1}$ and calcined at 600 °C for 6 h. The sample was named as $CeO_2$@$SiO_2$.

The CuO-$CeO_2$@$SiO_2$ catalysts were prepared by incipient wetness impregnation method. The as-prepared support was impregnated in the $Cu(COOH)_2{\cdot}3H_2O$ aqueous solution. Then, it was aged for 24 h and dried at 80 °C for 12 h. Finally, the solid was calcined at 600 °C for 6 h. The products were denoted as XCuO-$CeO_2$@$SiO_2$ catalysts. X before the symbol of CuO indicated quantity of CuO in the catalysts.

The 30CuO-$CeO_2$@$SiO_2$ catalyst was chosen as experimental sample and experienced the reduction-oxidation treatment in a tubular furnace as the following steps: (i) The sample was heated from room temperature to 200 °C, 250 °C or 300 °C with a ramp rate of 3 °C $min^{-1}$ and kept for 6 h in 10% $H_2$/Ar. (ii) The sample after reduction treatment was divided into two parts. One part was re-oxidized at 300 °C and another part was oxidized at 600 °C for 6 h in air. The obtained catalysts were marked as CuO-$CeO_2$@$SiO_2$-$R_YO_Z$. Y indicated the temperature of reduction (200, 250 or 300 °C). Z represented the temperature of re-oxidation (300 or 600 °C) after reduction treatment.

### 2.2. Catalyst characterization

X-ray powder diffraction was carried on a PANalytical Empyream X'pert PRO diffractometer by using Cu Kα source (λ = 0.15406 nm). The range of scan was between 10 °C and 80 °C. The average crystallite size was estimated according to Scherrer's equation.

Scanning electron microscopy images of the samples were obtained by a Hitachi S-4800 scanning electron microscope with an accelerating voltage of 15 kV. The samples were coated with a thin layer of gold and platinum before scanning.

Transmission electron microscopy images of the samples were taken on a FEI Tecnai $G^2$ F20 transmission electron microscope. The samples were dispersed into ethanol with ultrasonic treatment for 10 min, and a drop of the suspension was placed on a copper grid for TEM observation.

$N_2$ adsorption-desorption isotherms were achieved via a Quantachrome Autosorb-IQ adsorption analyzer at 77 K. Before each measurement, the sample was outgassed in vacuum at 200 °C for 12 h. The surface area was estimated by the Brunauer–Emmett–Teller method and the pore size distribution was calculated from the desorption branch using the Barrett–Joyner–Halenda method.

$H_2$ temperature-programmed reduction was conducted on a Micromeritics AutoChemII2920 equipped with a thermal conductivity detector. The samples were pretreated in a helium flow at 200 °C for 1 h and cooled to room temperature. The reduction profiles were collected in the 5% $H_2$/Ar mixture with a flow rate of 35 mL/min from room temperature to 800 °C.

X-ray photoelectron spectra were collected on a Perkin Elmer PHI 5000 ESCT System spectrometer with monochromatic Al Kα radiation source (1486.6 eV) for the analyses of the core level signals of Cu 2*p* and Ce 3*d*. During data processing of XPS spectra, binding energy values were referenced to C 1*s* peak (284.8 eV) from adventitious contamination layer.

### 2.3. Catalytic performance test

Catalytic performance tests were carried on a fixed-bed reactor at atmospheric pressure. A mixture gas containing 1.0 vol% CO, 1.0 vol% $O_2$, 50.0 vol% $H_2$ and $N_2$ balance was passed through the reactor filled with 100 mg catalyst. The space velocity was 40,000 mL $h^{-1}$ $g^{-1}$ and the reaction was operated from 35 to 235 °C. The inlet and outlet streams were measured using an online GC-2014C gas chromatograph equipped with a thermal conductivity detector. CO, $O_2$ and $N_2$ were separated by a 5A molecular sieve column, and $CO_2$ and $CH_4$ were separated by a TDX column. The conversion of CO ($C_{CO}$) and $O_2$ ($C_{O2}$) as well as selectivity of $CO_2$ ($S_{CO2}$) were calculated according to the following Eqs. (1), (2) and (3), respectively.

$$C_{CO}\ (\%) = ([CO]_{in} - [CO]_{out})/[CO]_{in} \times 100 \quad (1)$$

$$C_{O2}\ (\%) = ([O_2]_{in} - [O_2]_{out})/[O_2]_{in} \times 100 \quad (2)$$

$$S_{CO2}\ (\%) = C_{CO}/\lambda_{O2} \times 100 \quad (3)$$

In all the catalytic tests, λ = 2 was used, because this value was optimal for preferential oxidation of CO [26].

## 3. Results

### 3.1. Catalyst selection

#### 3.1.1. X-ray power diffraction

Fig. 1 shows XRD patterns of the CuO-$CeO_2$@$SiO_2$ catalysts with different CuO content. The diffraction peaks at 28.55°, 33.08°, 47.49° and 56.53° were indexed to cubic fluorite $CeO_2$ [27,28].

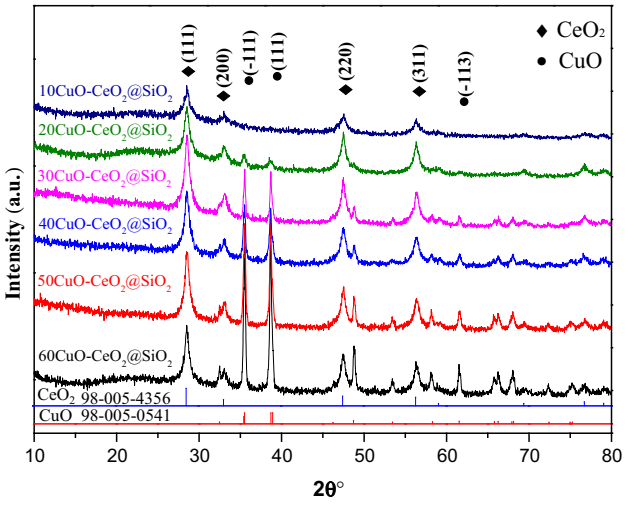


**Fig. 1.** XRD patterns of the CuO-$CeO_2$@$SiO_2$ catalysts.