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# Au/CuO–CeO<sub>2</sub> catalyst for preferential oxidation of CO in hydrogen-rich stream: Effect of CuO content

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## ABSTRACT

A series of Au/CuO–CeO<sub>2</sub> with various amounts of CuO was prepared. CuO–CeO<sub>2</sub> was prepared by co-precipitation and Au was loaded by deposition–precipitation. The aim of this study was to develop a catalyst which is highly active and selective in preferential oxidation of CO in hydrogen stream (PROX). These catalysts were characterized by N<sub>2</sub>-sorption, XRD, TEM, HR-TEM, and XPS. The PROX reaction was carried out in a fixed bed continuous flow reactor with a feed of CO: O<sub>2</sub>: H<sub>2</sub>: He = 1.33: 1.33: 65.33: 32.01 in volume ratios. The incorporation of copper ion into ceria lattice increased the oxygen storage capacity of ceria and enhanced the activity of the catalyst. The excess CuO would present on the surface of CeO<sub>2</sub>. Au particles were well dispersed well on the support and the particle size of gold was in the range of 2 and 4 nm. Au was the active species and CuO played the promoter role. Those CuO presented on the surface of CeO had negative effect for CO oxidation. The selectivity of oxygen reacting with CO increased with increasing CuO content. Adding suitable amount of CuO in Au/CeO<sub>2</sub> is beneficial for CO conversion and suppressing hydrogen oxidation in fuel cell operation condition.

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## Introduction

Fuel cells offer cleaner, more fuel-flexible and more-efficient alternatives to the combustion of gasoline and other fossil fuels. Using hydrogen fuel as power would avoid global warming gases being emitted into the atmosphere. The only emission from hydrogen fuel cells powered by renewable energy is pure water. The power produced will provide low carbon and low emission electricity. Currently, most of the

hydrogen is produced through the steam reforming of methane:



However, CO, one of the by-products in steam reforming reaction, is a poison to the platinum electrode of fuel cells operating at relatively low temperatures, PEM fuel cells, for example. Therefore, how to remove the existence of CO becomes an important issue in application of fuel cell. These gas purification processes include two steps: water-gas shift (WGS) reactions and preferential oxidation (PROX) reaction.

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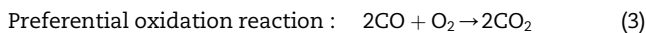
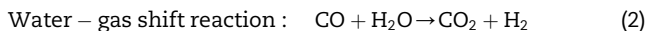
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WGS reactions can reduce the CO content to 0.5% and PROX reaction can make the existence of CO achieve the tolerance of PEM fuel cell which is 10 ppm.



Platinum catalyst has been proposed for the PROX reaction. However, the high cost of platinum is a block to commercialize this catalyst. Lower the cost is one of the considerations as developing PROX catalyst; as a result, gold is applied to replace platinum as the active metal. Gold is known as a kind of inert substance except it is of nanoparticles state. Haruta [1] reported that gold nanoparticles show good activity as they are supported on metal oxide support. The preparation method and the choice of support cause a large influence on the activity of catalysts. The particle size was decided by the preparation situation, and the suitable metal oxide can greatly promote the activity [1–10].

The metal oxide support can be classified into two groups: active support and inert support [11]. The active support is superior because they are reducible and with ability to provide reactive oxygen, which can served as oxygen reservoir. In other words, they provide additional sites at the interface for the adsorption of the reactant close to the gold site [12–14]. CeO<sub>2</sub> is one of the supports with high oxygen storage capacity and has been used as the support for noble metals [15–29]. However, Au/CeO<sub>2</sub> is not very selective in PROX reaction. CuO has been used as a promoter of Au/TiO<sub>2</sub> to improve the performance of the catalyst in PROX. Therefore CuO was chosen as a promoter for Au/CeO<sub>2</sub> in this study. CuO could incorporate into CeO<sub>2</sub> lattice structure and enhance the oxygen storage [29]. This is believed to be beneficial to enhance the activity of Au in PROX reaction. The aim of this study was to investigate the effect of CuO content in Au/CeO<sub>2</sub> for PROX.

## Experimental

### Catalyst preparation

A series of CuO–CeO<sub>2</sub> are been prepared by co-precipitation. Co-precipitation method made Cu and Ce precipitate at the same time and mix well [29]. After calcination in air, it was expected that more Cu would incorporate into the lattice structure of CeO<sub>2</sub>. Copper nitrate and cerium nitrate were dissolved in distilled water in a beaker, 25% NH<sub>4</sub>OH was added as the precipitation agent to adjust the pH value to 10. After aging for 8 h, the precipitate was filtered and the filtration cake was washed several times to remove nitrate ions. The filtration cake was dried overnight in air at 80 °C for 8 h, and subsequently calcined at 550 °C for 4 h in air.

Au was loaded on the CuO–CeO<sub>2</sub> support with deposition–precipitation (DP) method. DP method was the most common method to prepare gold catalysts as it is easy to obtain gold particles less than 5 nm in size. An aqueous solution of HAuCl<sub>4</sub> (2.55 × 10<sup>−3</sup> M) was added at a rate of 10 ml/

min into the solution containing suspended support under vigorous stirring and the temperature of the solution was maintained at 65 °C. NH<sub>4</sub>OH was used to adjust the pH value of the solution at 8. After aging for 2 h, the precipitate was filtered and the filtration cake was washed with hot water until no chloride ions were detected using 0.1 M AgNO<sub>3</sub> solution. Finally, the filtration cake was dried overnight in air at 80 °C overnight, and then calcined at 180 °C for 4 h. The nominal amount of gold loaded on the support corresponded to 1 wt. %. Au/CeO<sub>2</sub> and Au/CuO were prepared by the same method.

### Characterization

The catalysts were characterized by the following techniques: Brunauer–Emmett–Teller (BET) specific surface area by N<sub>2</sub>-sorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM), and X-ray photoelectron spectroscopy (XPS).

#### BET surface area

The surface area of the samples was measured using a Micromeritics ASAP 2010 by Brunauer–Emmett–Teller (BET) method for relative pressures in the range P/P<sub>0</sub> = 0.05–0.3. Prior to the experiments, the samples were evacuated at 120 °C for 8 h at the vacuum pressure below 1 × 10<sup>−5</sup> Torr.

#### XRD

XRD analysis was performed using a Siemens D5000 powder diffractometer using Cu K<sub>α1</sub> radiation (0.15405 nm) at a voltage and current of 40 kV and 40 mA, respectively. The sample was scanned over the range of 2θ = 20–70° at a rate of 0.05°/min to identify the crystalline structure.

#### TEM and HR-TEM

The morphologies and particle sizes of the samples were determined by TEM on a JEM-2000 EX II operated at 120 kV and HR-TEM on a JEOL JEM-2010 operated at 160 kV. Initially, a small amount of sample was placed into the sample tube filled with a 95% ethanol solution and after agitating under ultrasonic environment for 3 h, one drop of the dispersed slurry was dipped onto a carbon-coated copper mesh (300#) (Ted Pella Inc., CA, USA), and dried in vacuum overnight. Images were recorded digitally with a Gatan slow scan camera (GIF). Based on the several images of TEM or HRTEM, more than 100 particles were counted and the size distribution graph was made.

#### XPS

The XPS spectra were recorded with a Thermo VG Scientific Sigma Prob spectrometer. The XPS spectra were collected using Al K<sub>α</sub> radiation at a voltage and current of 20 kV and 30 mA, respectively. The base pressure in the analyzing chamber was maintained in the order of 10<sup>−9</sup> torr. The spectrometer was operated at 23.5 eV pass energy and the binding energy was corrected by contaminant carbon (C1s = 285.0 eV) in order to facilitate the comparisons of the values among the catalysts and the standard compounds. Peak fitting was done

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