

# Selective oxidation of CO in excess hydrogen over CuO/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts

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## Abstract

Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> ( $x=0.1-0.5$ ) mixed oxides were prepared as supports of CuO/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts. They were characterized and used in the selective oxidation of carbon monoxide (CO) in excess hydrogen. An appropriate amount of zirconium incorporated into CeO<sub>2</sub> not only increased the mobility of lattice oxygen but also promoted the activity of the selective CO oxidation. The promotion of CO oxidation was weakened as the amount of Zr<sup>4+</sup> increased above 10% ( $1-x > 0.1$ ). The temperature ( $T_{100}$ ) of 7%CuO/Ce<sub>0.9</sub>Zr<sub>0.1</sub>O<sub>2</sub> for complete conversion was about 10 degrees lower than that of 7%CuO/CeO<sub>2</sub> (378 K), and the selectivity achieved was nearly 100%. The activity of the 7%CuO/Ce<sub>0.9</sub>Zr<sub>0.1</sub>O<sub>2</sub> catalyst was weakened in the feed in the presence of CO<sub>2</sub> and H<sub>2</sub>O, but the selectivity and stability of the catalyst were maintained. The 7%CuO/Ce<sub>0.9</sub>Zr<sub>0.1</sub>O<sub>2</sub> catalyst exhibited not only good activity that was comparable with that of the noble metal catalyst of 5%Pt/Al<sub>2</sub>O<sub>3</sub> but also good selectivity of much greater than 5%Pt/Al<sub>2</sub>O<sub>3</sub>.

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## 1. Introduction

The development of efficient catalysts for the selective oxidation of carbon monoxide (CO) in the presence of excess hydrogen is a current challenge in research on the heterogeneous catalysis of the preparation of H<sub>2</sub> for use in a polymer electrolyte membrane fuel cell (PEMFC) [1,2]. Hydrogen is used as a fuel in the PEMFC system and ideally the only reaction product is H<sub>2</sub>O. Hydrogen is generally generated from hydrocarbons or methanol by steam/autothermal reforming or partial oxidation followed by a water-shift reaction [3–6]. Typical effluents from such a process contain 0.3–1% of CO in an excess of H<sub>2</sub> (40–75%) and

20–25% CO<sub>2</sub>. CO must be removed to avoid poisoning of the anode electro-catalysts [7,8]. CO levels must be reduced to below 100 ppm for use in PEMFC. The CO concentration can be reduced to acceptable levels by catalytic methanation, Pd-based membrane purification and catalytic selective CO oxidation [7–9]. Of these methods, the selective oxidation of CO with O<sub>2</sub> appears to be the simplest and most effective method for removing CO. The most important requirements of catalysts of selective oxidation are a high oxidation rate of CO and a high selectivity with respect to the side oxidation reaction of H<sub>2</sub>. Such catalysts should also be able to tolerate the presence of CO<sub>2</sub> and H<sub>2</sub>O.

The catalysts proposed in the literature for the selective oxidation of CO are noble metal based, including alumina-supported Pt-group metal catalysts [10–14] and metal oxide-supported Au catalysts [15–19].

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Gold based catalysts have been found to be markedly more active catalysts than Pt-group metal catalysts at low temperatures ( $< 393$  K), but not as resistant to deactivation by  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [20]. None of these catalysts can prevent significant losses of hydrogen by oxidation.  $\text{CuO-CeO}_2$  mixed oxide catalysts have been reported to be very active catalysts in the oxidation of CO with a specific activity several orders of magnitude higher than that of conventional Cu-based catalysts, comparable to Pt-based catalysts [21,22]. Mixed oxides of  $\text{CuO-CeO}_2$  have recently been proposed as good candidates for the selective removal of CO from reformat streams [20,23]: they can be used in the temperature range of 373–423 K with a selectivity of 95–90% for complete conversion; they are more active and significantly more selective than Pt-based catalysts at a lower reaction temperature; they are less active but much more selective than Au-based catalysts. The use of the mixed oxide  $\text{CuO-CeO}_2$  for CO oxidation has recently attracted much attention.

$\text{CuO}$  supported on  $\text{CeO}_2$  enhances CO oxidation through a synergistic effect. Cerium oxide is well known to have a high oxygen exchange capacity [24,25], which is related to the capacity of cerium to change oxidation states reversibly between  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  by receiving or giving up oxygen [26]. CO oxidation is thought to proceed at the metal-support interfacial perimeter. The reduction of  $\text{CeO}_2$  has been demonstrated to proceed via a surface reaction that involves the reductant CO [27,28]. Hence, the oxygen from the support oxidizes the reductant adsorbed on the metal particle at the interface [29,30], and the oxygen vacancy is then replenished by  $\text{O}_2$ . Incorporating zirconium into  $\text{CeO}_2$  has been recently reported to improve the oxygen storage capacity, the redox property and the thermal resistance of the resulting mixed oxide [31,32]. In the mixed oxide of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ,  $\text{Ce}^{4+}$  is partially substituted for  $\text{Zr}^{4+}$  in the lattice of  $\text{CeO}_2$ , forming a solid solution. Hori et al. [31] found that the beneficial effects of  $\text{ZrO}_2$  were pronounced in solid solutions of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x = 0.5-0.6$ ) that had oxygen capacities three to five times higher than that of the pure  $\text{CeO}_2$ .  $\text{Zr}^{4+}$  increased the capacity of redox property, so  $\text{CuO}$  supported on  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  was expected to enhance CO oxidation. Martinez-Arias et al. [33] investigated the catalytic behavior of  $\text{CuO/CeZrO}_4$  ( $\text{Zr/Ce} = 1$ ) and  $\text{CuO/CeO}_2$  catalysts in CO oxidation, and found that the CO oxidation activity of  $\text{CuO/Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  was weaker than that of  $\text{CuO/CeO}_2$ . However, preliminary studies revealed that the  $\text{CuO/Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x < 0.2$ ) catalysts enhanced CO oxidation. This study examines

the selective oxidation of CO over  $\text{CuO/Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts.

$\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  mixed oxides were prepared and used as supports for preparing  $\text{CuO/Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts. X-ray diffraction (XRD), temperature-programmed reduction (TPR) and pulse adsorption of CO were used to characterize the catalysts. The goal of this study is to evaluate the activities and selectivities of a series of  $x\%\text{CuO/Ce}_x\text{Zr}_{1-x}\text{O}_2$  (with  $x = 0.1-0.5$ ) catalysts in the selective oxidation of CO in excess hydrogen. The effects of  $\text{Zr}^{4+}$  on the redox property and the activity of CO oxidation were examined. The best sample was also tested in the feed in the presence of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and compared with the precious metal catalyst, 5%Pt/ $\text{Al}_2\text{O}_3$ .

## 2. Experimental

### 2.1. Preparation of catalysts

The  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  mixed oxides were prepared by coprecipitation. Sufficient  $\text{NH}_4\text{OH}$  was added to a mixed aqueous solution of cerium nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) and zirconium oxynitrate ( $\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ ). The precipitate was washed several times in deionized water, and then dried overnight at 393 K. The resulting powders were calcined at 923 K for four hours in air. The  $\text{CuO/Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts (with  $x = 0.1-0.5$ ) were prepared by the incipient impregnation of an aqueous solution of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), dried at 393 K overnight and then calcined at 923 K for 4 h in air.

### 2.2. Characterization of catalysts

The BET surface areas and the pore size distributions were determined using an ASAP 2010 apparatus with nitrogen adsorption at 77 K. XRD patterns were collected using a Siemens-500 diffractometer at 40 kV and 30 mA, using  $\text{Cu K}\alpha$  radiation ( $\lambda_\alpha = 0.1542$  nm).

TPR measurements were made in a flow system that consisted of a quartz micro-reactor attached to a thermal conductivity detector. The catalyst (60 mg) was pretreated at 673 K for one hour under a stream of argon, and then cooled to room temperature. It was then reduced by increasing the temperature to 1473 K at a rate of 10 K/min in a stream of 10%  $\text{H}_2/\text{Ar}$ . The water thus produced was trapped using a 3A molecular sieve; hydrogen consumption was monitored using a thermal conductivity detector.

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