



# Mesoporous ceria-zirconia supported cobalt oxide catalysts for CO preferential oxidation reaction in excess H<sub>2</sub>

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## ABSTRACT

Mesoporous Co<sub>3</sub>O<sub>4</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (x = 0.75, 0.85, 0.95, 1) catalysts were synthesized by surfactant-assisted co-precipitation with subsequent incipient wetness impregnation (SACP-IWI) method. The prepared mesoporous ceria-zirconia supported cobalt oxide catalysts were used to catalyze CO preferential oxidation (PROX) reaction to eliminate the trace CO from H<sub>2</sub>-rich gases. The effects of structure-directing agent (SDA) type, atomic ratio of Ce/(Ce + Zr), cobalt oxide loading and reaction parameters on the catalytic properties for CO PROX reaction in excess H<sub>2</sub> were investigated. Moreover, the various characterization techniques like N<sub>2</sub> adsorption/desorption, X-ray diffraction (XRD), H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR), NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD), Fourier-Transform infrared spectroscopy (FT-IR) were employed to study the relationship between catalyst nature and catalytic properties. The results of N<sub>2</sub> adsorption/desorption and X-ray diffraction patterns indicate that catalysts prepared by using cationic surfactant cetyltrimethylammonium bromide (CTAB) as SDA possess an ordered mesoporous architecture and exhibit much better catalytic activity compared with those prepared by using anionic surfactant ammonium dodecylbenzenesulfonate (ADBS) as SDA. The residual sulfur from ADBS was demonstrated to be the main reason for the much worse catalytic performance by the characterization results of FT-IR and NH<sub>3</sub>-TPD. Results show that the developed Co<sub>3</sub>O<sub>4</sub>/meso-Ce<sub>0.85</sub>Zr<sub>0.15</sub>O<sub>2</sub> catalysts by SACP-IWI method with CTAB as SDA show an outstanding catalytic performance for CO PROX reaction, which mainly depends on the redox behavior of catalyst and cobalt oxide dispersion affected by the ceria-zirconia support feature, atomic ratio of Ce/(Ce + Zr) of support and cobalt oxide loading.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have become the most attractive clean alternatives to conventional combustion of fossil fuels to generate energy with high efficiency and power density but low operating temperature [1–4]. The hydrogen used in PEMFCs generally comes from reforming streams of hydrocarbon and alcohols, which may still contain 0.5–2% CO even after undergoing the high and subsequent low temperature water-gas shift (WGS) reactions. However, the trace amount of CO can easily poison the anode materials of PEMFCs. The allowed CO concentrations are defined as less than 10 ppm for a Pt anode and less than 100 ppm for a CO-tolerant alloy anode [5,6]. Therefore, various strategies have been developed to remove the trace amount of CO from the H<sub>2</sub>-rich gases. Among them, the CO PROX reaction has been considered as the simplest and most effectual method for purifying H<sub>2</sub>-rich gases.

The key point of this method is to find catalysts having good activity and selectivity for CO oxidation in the presence of H<sub>2</sub> at a wide temperature-window, high tolerance towards CO<sub>2</sub> and H<sub>2</sub>O those exist in the reformed fuel, but low activity for the undesired side reactions like H<sub>2</sub> oxidation, reverse WGS, methanization, etc.

Catalysts reported for CO PROX reactions are mainly precious metal catalysts, such as Au, Pt, Ru and Rh, exhibiting better low-temperature activity in comparison with base metal catalysts [7–12]. Due to the high cost and limited availability of precious metals, the catalysts based on non-precious metals are considered as promising alternatives for CO PROX reaction in excess H<sub>2</sub>. CuO-CeO<sub>2</sub> [13–15] and CuO/CeO<sub>2</sub> [16,17] systems, especially, were well studied and the good catalytic performance for CO PROX reaction had been achieved. Nowadays, many reports focus on Cu based catalysts for CO PROX reaction, and have achieved fruitful results. But some shortcomings such as less anti-H<sub>2</sub>O, CO<sub>2</sub> capability, not satisfactory CO selectivity and also narrow temperature window, etc. remain to be overcome. Studies on the other non-precious metals gain increasing attentions. Co based catalysts with outstanding catalytic properties have shown better low-temperature activity,

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selectivity and the H<sub>2</sub>O resistance than CuO<sub>x</sub>, which can be considered as a promising candidate for the CO PROX reaction in excess H<sub>2</sub> [18–23]. Co<sup>3+</sup> as the active site provides its lattice-oxygen to the CO ultimately forming a Co<sup>2+</sup> that can be re-oxidized with oxygen [20,24]. While during the CO PROX process, the H<sub>2</sub> in feed gets high-valence cobalt reduced to low-valence ones [25,26], which is not active for CO PROX reaction. Supported on a metal oxide carrier is a feasible way for Co<sup>3+</sup> to be kept at its high-valence state in a H<sub>2</sub> atmosphere [27]. The support materials could essentially play a significant role in modifying the formation of active Co metal species via metal–support interaction. Many reports have shown that the supported cobalt catalysts possess excellent redox behaviors [28–31]. The CeO<sub>2</sub>–ZrO<sub>2</sub> composite oxide system, for its peculiar optical and magnetic properties and especially the unexpected oxygen mobility, has been supposed to be a candidate for support to stabilize the high-valence cobalt species. In our previous studies [32], cobalt oxide supported on CeO<sub>2</sub>–ZrO<sub>2</sub> nanoparticle showed promising catalytic performance for CO PROX reaction in the presence of H<sub>2</sub>. Nevertheless, the low specific surface area of nanoparticle as support is its essential limitation, which is unfavorable for the dispersion of active species. To prepare ceria-zirconia composite oxide with mesoporous structure is an efficient avenue to enlarge its specific surface area. Moreover, the morphologies have been found to significantly affect the oxygen vacancy formation energy of support, resulting in different catalytic properties [16]. Herein, we prepared the different mesoporous ceria-zirconia composite oxides by SACP method with two kinds of SDA (CTAB and ADBS), and then supported cobalt oxide to obtain a series of Co<sub>3</sub>O<sub>4</sub>/meso-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts. The effects of SDA (cationic and anionic surfactant), Ce/(Ce + Zr) atomic ratio and cobalt oxide loading amount on the catalyst nature and the catalytic performance for CO PROX reaction in excess H<sub>2</sub> were investigated. In addition, the influence of reaction parameters like CO<sub>2</sub> and H<sub>2</sub>O in the feed, gas hourly space velocity (GHSV) and O<sub>2</sub> concentration on CO PROX reaction was also investigated. Characterizations including XRD, N<sub>2</sub> adsorption/desorption, FT-IR, H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD were employed to investigate the relationship between physicochemical properties of catalysts and catalytic performance. In the present paper, we find out that the prepared catalysts employing CTAB as SDA possess ordered mesoporous architecture and show promising catalytic performance for CO PROX reaction in excess H<sub>2</sub>. However, the supported cobalt oxide catalyst with ceria-zirconia as support using the ADBS as SDA owns much worse activity for CO PROX reaction. The negative effect of anionic ADBS as SDA was found to be mainly corroborated to the residual sulfur, which gives an acidic nature to catalyst that is apt to break the equilibrium of surface acidic and basic sites, resulting in very low activity for CO oxidation. The prepared Co<sub>3</sub>O<sub>4</sub>/meso-Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (CTAB as SDA) could be effective catalysts for eliminating CO from H<sub>2</sub>-rich gases, and the catalytic performance is dependent on the redox behavior and Co<sub>3</sub>O<sub>4</sub> dispersion, affected by the Ce/(Ce + Zr) ratio and cobalt oxide loading.

## 2. Experimental

### 2.1. Catalysts preparation

The Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> ( $x = 0.75, 0.85, 0.95, 1$ ) composite oxides were prepared by the SACP method. Typically, 17 mmol of ammonium cerium nitrate (Sinopharm, AR) and 3 mmol of zirconium nitrate (Tianjin Damao, AR) were dissolved in deionized water. A certain amount of CTAB (Kermel, AR) was added to 25 ml of deionized water to give a clear homogeneous solution. Then, the two solutions were mixed under continuously stirring for 2 h. Afterward, pre-determined amount of ammonium solution (25%) was added

drop by drop under vigorous stirring, leading to a final pH value of 11. After precipitation, the gelatinous pale yellow mixture was stirred for further 4 h and subsequently transferred to Teflon autoclaves, which were kept at 105–120 °C for 3 d. The solid product was filtered, washed with deionized water and ethanol, subsequently dried at 105 °C overnight, and then calcined in a muffle furnace in air with  $T_{\text{sup}}$  at 550 °C for 6 h, where  $T_{\text{sup}}$  was denoted as the calcination temperature for preparing mesoporous ceria-zirconia composite oxide supports. Preparation of the other Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> composite oxides with different Ce/(Ce + Zr) atomic ratios underwent the same way but only changing the relative amount of Ce and Zr precursors. Ce<sub>0.85</sub>Zr<sub>0.15</sub>O<sub>2</sub> composite oxide was also synthesized using ADBS as SDA.

The mesoporous Co<sub>3</sub>O<sub>4</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> ( $x = 0.75, 0.85, 0.95, 1$ ) catalysts with various cobalt loadings (4 wt.%, 8 wt.%, 12 wt.%, 16 wt.%, 20 wt.% and 27 wt.%) were prepared by IWI method using cobalt nitrate (Tianjin Bodi, AR) as Co precursor. After each impregnation step, the sample was dried at 105 °C for 2 h to evaporate the solvent, and the final sample was calcined at 450 °C in air for 5 h.

### 2.2. Catalysts characterization

The BET specific surface area, total pore volume and pore size distribution were obtained from the adsorption and desorption isotherms of nitrogen at –196 °C using a Quantachrome Autosorb-1 apparatus. FT-IR spectra were collected in the wave number range 4000–400 cm<sup>-1</sup> on EQUINOX-55 Fourier Transform Infrared Spectrometer (BRUKER). The powder XRD experiments were carried out on Rigaku Automatic X-ray Diffractometer (D/Max 2400) equipped with a Cu K $\alpha$  source ( $\lambda = 1.5406 \text{ \AA}$ ). The XRD patterns were recorded from 0.5° to 80° with a step width of 0.02°. The crystallite parameters were estimated based the Scherrer Formula over multiple characteristic diffraction peaks by the MDI Jade5 software.

H<sub>2</sub>-TPR experiments were performed in an in-house constructed system equipped with a thermal conductivity detector (TCD) to measure H<sub>2</sub> consumption. 50 mg sample was pretreated under a 2.5 vol.% O<sub>2</sub>/Ar flow (30 ml min<sup>-1</sup>) at 450 °C (the same as the calcination temperature for catalyst preparation) for 30 min, followed by cooling to room temperature in an Ar flow (30 ml min<sup>-1</sup>). After that, it was reduced with a 10 vol.% H<sub>2</sub>/Ar mixture (30 ml min<sup>-1</sup>) by heating up to 800 °C at a ramp rate of 10 °C min<sup>-1</sup>.

The acidic properties of the catalysts were measured by an in-house constructed system equipped with a thermal conductivity detector (TCD) to monitor desorbed NH<sub>3</sub>. After pretreated with Ar at 450 °C (the same as the calcination temperature for catalyst preparation) for 30 min, the reactor was cooled down to about 150 °C, and then saturated with pulse introduction of NH<sub>3</sub>. The sufficient saturation was checked by analyzing the outlet gas via a TCD. Afterwards, the sample was subjected to programmed-heating in an Ar flow with a ramp rate of 10 °C min<sup>-1</sup>. Thermal desorption of NH<sub>3</sub> was recorded by TCD.

### 2.3. Catalytic performance tests

The catalytic activity tests for CO PROX reaction in H<sub>2</sub>-rich gases were performed in a stainless steel, fixed bed continuous-flow reactor (6 mm O.D.) with 100–200 mg of catalyst held between two quartz wool plugs. The reaction feed consisted of 1.0 vol.% CO, 1.0 vol.% O<sub>2</sub>, 50 vol.% H<sub>2</sub> and Ar balance. Samples were pretreated in 2.5 vol.% O<sub>2</sub>/Ar flow at 300 °C for 30 min. The temperatures were measured by using K-type thermocouples and controlled by a PID controller. The analysis of the effluent gas was performed using a gas chromatograph on-line with a molecular sieve column and a Poropak Q column. The CO and CO<sub>2</sub> signals were detected by the FID detector after the gas passing through a methanizer. 10 vol.%

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