



Identification of the nano/micro structure of CeO₂(rod) and the essential role of interfacial copper-ceria interaction in CuCe(rod) for selective oxidation of CO in H₂-rich streams



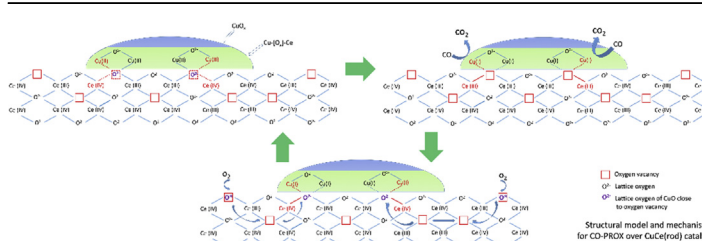
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HIGHLIGHTS

- CeO₂(rod) behaves as a hexagonal prism exposed four {111} and two {100} planes.
- CeO₂(rod) is formed by the first oriented attachment and subsequent Ostwald ripening.
- Copper oxides are highly dispersed on CeO₂(rod) with different hydrothermal time.
- The same architecture of Cu-Ce interaction with different strength has been formed.
- Strongly bound Cu-[O_x]-Ce promotes the catalytic activity of CuCe(rod) for CO-PROX.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 January 2017
Received in revised form
8 June 2017
Accepted 20 June 2017

Keywords:

Hydrogen purification
CO selective oxidation
CuCe(rod) catalyst
Microstructure
Highly dispersed CuO
Strongly bound Cu-[O_x]-Ce

ABSTRACT

CeO₂(rod) has been found to be exposed four {111} planes and two {100} planes with a hexagonal cross section, and the growth mechanism follows to the oriented attachment of the cube-like basic grains with a [110] growth direction and the subsequent Ostwald ripening, corresponding to the increasing lateral size and longitudinal size with prolonging the hydrothermal time. Equal amount of copper oxide totally highly distributed on the surface of CeO₂(rod) supports with different abundance of oxygen vacancies facilitate to produce the strongly bound Cu-[O_x]-Ce species to different degrees (supported by XPS, H₂-TPR and in situ DRIFTS results), which is encouraged by prolongation of hydrothermal time of CeO₂(rod) supports. The essential role of interfacial Cu-Ce interaction in CuCe(rod) catalysts for CO-PROX was identified by the enhanced catalytic performance of CuCe(rod)-48h, on account of much stronger Cu-Ce interaction generated in it. Moreover, we proposed a potential structural model of strongly bound Cu-[O_x]-Ce to interpret the synergetic effect of copper and ceria species in CuO/CeO₂ catalysts and generalized the possible reaction mechanism for CO-PROX over the CuCe(rod) catalyst.

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1. Introduction

Nowadays, the utilization of traditional fossil energy, mainly in power generation and engine combustion processes, has given rise to many problems such as the energy shortage and air pollution.

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Polymer electrolyte membrane fuel cells (PEMFCs) presents great potential for applying to both the residential power-generation and mobile power source due to its high energy conversion efficiency and pollution-free features [1–3]. However, hydrogen generated by the steam reforming of hydrocarbons or bioethanol followed by low-temperature water-gas shift (WGS) reaction always contains approximately 0.5–1.0 vol % CO, which cannot meet the demand of the ideal feed gas for PEMFCs due to that the little CO would poison the Pt anode and reduce the surface Pt sites for H₂ adsorption/dissociation and oxidation and thus decrease the efficiency of PEMFCs [4,5]. Selective oxidation of CO with the introduction of a little oxygen in the hydrogen rich gas (CO-PROX) has been taken as an efficient and convenient method to eliminate the CO traces below 100 ppm [1,6,7]. In order to achieve a high CO conversion at the moderate temperature (between the WGS temperature and the operation temperature of PEMFCs) with high selectivity, many efforts have been devoted to develop an ideal catalyst for CO-PROX. For example, supported noble metals catalysts (Au, Pt, Ru) [8–10] were most frequently investigated, however, the high cost and low selectivity hindered their practical application. Fortunately, some transition metal supported catalysts especially ceria-supported CuO catalysts have attracted attention because of the unique properties of ceria for oxygen storage, ready reducibility, and its ability to firmly anchor Cu, reducing its tendency to sinter, which exhibit superior activity, selectivity and resistance to CO₂ and H₂O for CO-PROX and simultaneously satisfy the economical requirement based on their low cost [11,12].

The oxygen storage capacities, redox properties and surface exposed plane can be tailored through controllable synthesis of CeO₂ nanoparticles with different shapes. CeO₂ nanorods display higher oxygen storage capacity and exhibit higher CO conversion at lower temperature [13]. In previous work [14], we have investigated the morphology effect of ceria on CuO/CeO₂ catalysts for CO-PROX. CuO/CeO₂-rod catalyst exhibits higher catalytic performance with the much lower T_{50%} and a broader operating temperature window in CO-PROX than CuO/CeO₂-plate and CuO/CeO₂-cube, which might as a consequence of its higher specific surface area, different exposed crystal facet, abundant oxygen vacancies and more copper species strongly interacted with ceria species.

However, concerning about the catalytic processes, active species or sites and structure-activity relationship of CO-PROX over CuO/CeO₂ catalysts, there exists multiple interpretations by different laboratories. Gamarra et al. reported that CO oxidation takes place at the interfacial range of the dispersed copper oxide entities and CO conversion rate can be estimated by the Cu⁺-carbonyls, which is affected by interactions with ceria support and therefore the copper oxide entities located at the interface of the catalysts. As for H₂ oxidation, it is proceeded by the partial reduced dispersed copper oxide particles [6,15,16]. Zhang et al. found that the active redox oxygen site in a mixed Cu and Ce oxide catalyst is the first oxygen neighbor of Cu(II) species at the interface between Cu and Ce, which is removed by the reduction of Cu(II) to Cu(I) to oxidize CO and re-generable by reducing the nearby Ce⁴⁺ to Ce³⁺ [17]. Yao et al. by means of a novel device combining time-resolved XANES and DRIFTS with parallel time-resolved X-ray diffraction, probed the redox behavior of CuO/CeO₂-rod catalysts prepared by incipient wetness impregnation under CO reduction, CO oxidation and CO/O₂ cycling reactions. A strong copper - ceria synergistic effect and a strong correlation between surface Cu(I) species and the catalyst activity for the CO oxidation reaction have been observed in CuO/CeO₂-rod catalysts [18]. However, Wang et al. reported that the highly dispersed CuO_x cluster rather than the strong interaction of Cu-[O_x]-Ce structure, is the more crucial active species in Cu-Ce-O system for CO-PROX, via studying a series of CuO/CeO₂-rod catalysts synthesized by deposition-precipitation

methods with the assistance of in situ XANES/EXAFS techniques [19].

In this passage, we focus our attention on catalysts generated by dispersing CuO on a series of CeO₂ nanorods, paying particular attention to the synergistic effect of the well constrained ceria support with the supported Cu. A series of ceria nanorods with the same exposed crystal faces but different surface defects were obtained by means of tuning the hydrothermal time. Copper-ceria nanorod catalysts with different interfacial Cu-Ce interactions were synthesized with an ethanol-thermal approach by dispersing copper oxide species on the series of CeO₂(rod) supports. XRD Rietveld refinement and HRTEM were used to characterize the texture and structure properties. XPS, H₂-TPR and in situ DRIFTS were employed to characterize the surface element distribution, redox properties and the evolution of active Cu⁺-carbonyl. It is beneficial for us to figure out the role of the interfacial Cu-Ce interaction in copper-ceria catalyst for CO-PROX, and draw some inferences about the reaction mechanism of CuO/CeO₂ catalysts for CO-PROX.

2. Materials and methods

2.1. Synthesis of CeO₂

CeO₂(rod) with different lengths and diameters were synthesized through a hydrothermal method with different hydrothermal time. Specifically, 4 mmol of Ce(NO₃)₃·6H₂O dissolved in 10 mL H₂O was dropwise added to 70 mL sodium hydroxide solution which contained 19.2 g of NaOH. The mixed solution was vigorously stirred for about 30 min and transferred to a Teflon-lined autoclave and then suffered to hydrothermal treatment at 100 °C for 7h, 15 h, 24 h and 48 h, respectively for CeO₂(rod)-7h, CeO₂(rod)-15h, CeO₂(rod)-24h and CeO₂(rod)-48h.

After hydrothermal treatment or precipitation, the obtained four precipitates were separated by centrifugation, washed three times in turns by deionized water and ethanol respectively, and dried at 80 °C overnight.

2.2. Synthesis of CuO/CeO₂

The CuCe(rod) catalysts were synthesized by an ethanol-thermal approach [20]. 0.4 g of prepared ceria supports were added to 8 mL of ethanol solutions which contains 0.1167 g of Cu(NO₃)₂·3H₂O under vigorously stirring. After stirring for 40 min, the obtained slurries were transferred to a Teflon-lined autoclave and then subjected to a thermal treatment at 120 °C for 12 h. After cooling to room temperature, the samples were separated by centrifugation, washed with deionized water for 3 times, dried at 80 °C overnight and calcined at 500 °C for 2 h in air. The four catalysts were named as CuCe(rod)-48h, CuCe(rod)-24h, CuCe(rod)-15h and CeO₂(rod)-7h. The copper content of all the catalysts was fixed at 7.0 wt %.

2.3. Catalytic performance tests

The catalytic reaction of the catalysts for CO-PROX was carried on a quartz tubular micro-reactor under atmospheric pressure. The reaction gas of 1.0% CO, 1.0% O₂, 50% H₂ and Ar in balance with a total flow rate of 100 mL/min went through 100 mg of the catalyst with 60–80 mesh diluted with equal volume of the same meshed inert α -alumina. The corresponding space velocity is 60,000 mL g⁻¹ h⁻¹.

The component of the outlet gases was determined by an on-line gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) used Ar (highly purified, 99.999%) as carrier gas. The outlet gases went through a

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