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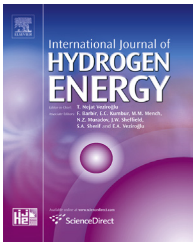

Synthesis of mesoporous Co–Ce oxides catalysts by glycine-nitrate combustion approach for CO preferential oxidation reaction in excess H_2

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ABSTRACT

Preferential oxidation of CO (CO-PrOx) is an important step to meet the need of the proton exchange membrane (PEM) fuel cell without the Pt anion poison. A glycine-nitrate approach was used for the synthesis of Co/CeO_2 nanoparticle for preferential oxidation of CO, which a precursor solution was prepared by mixing glycine with an aqueous solution of blended nitrate in stoichiometric ratio. Then the glycine-mixed precursor solution was heated in a beaker for producing nanosized porous powders. Catalytic properties of the powders were investigated and results illustrate that the Co-loading of 30 wt.% catalysts exhibits excellent catalytic properties. Various characterization techniques like X-ray diffraction, SEM, BET, Raman and TPR were used to analyze the relationship between catalyst nature and catalytic performance. The X-ray diffraction patterns and SEM micrographs indicate that catalysts prepared by glycine-nitrate combustion own mesopore structure. The BET, Raman and TPR results showed that the high activity of the 30 wt.% Co-loading of Co/CeO_2 catalysts is related to the high BET surface and the strongly interaction between fine-dispersed Co species and CeO_2 support.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) has shown a high potential for widespread use as power-generation device due to the advantage of highly efficiency and environment-friendly, especially for vehicle application [1]. The hydrogen generated by steam reforming or partial oxidation of hydrocarbons followed by the water-gas shift (WGS) reaction, contains 0.5–5% CO, which can cause a serious poison of the Pt-based PEMFC electrode catalysts. Thus CO content of hydrogen fuel must be reduced to an acceptable level below 100 ppm, and preferably, 10 ppm to prevent poisoning of Pt–Ru electrocatalysts used as anode materials before it enters a fuel cell.

Currently, the preferential oxidation of CO is considered to be the most efficient and cost-effective method for deep removal of CO. Noble material catalysts, including Pt, Ru, Rh,

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Pd [2–5] and Au [6–8], have been considered and intensively studied, which have shown high activities and good stabilities in CO-PrOx. However, the high cost of noble metal catalysts limited the availability of the industrial application, and some other shortcomings such as the rapid selectivity decrease of CO oxidation at high reaction temperatures, and low tolerance to H_2O and CO_2 remain to be solved. Many researchers have been devoted to developing low-cost techniques for catalyst synthesis. Transition metal-based catalysts (Co, Cu, and Mn) have attracted much attention in recent years [9,10]. Co_3O_4 has been reported to be one of the most promising non-noble metal oxide catalysts for CO oxidation without H_2 in the reaction gas stream at low temperatures [11–13]. It has been reported that Co_3O_4 nanorods not only catalyzed CO oxidation at temperatures as low as −77 °C but also remain stable in a moist stream of normal feed gas [14]. However, very few report about Co-based catalysts for the CO-PrOx in H_2-rich steam. Meanwhile, Fluorite oxides, such as CeO_2 and ZrO_2, not only have a high oxygen storage capacity and high oxygen vacancy properties, which are considered as appropriate candidates for oxidation process [15–17], but also enhance and stabilize the dispersion of transition metal oxides [12]. In the process of catalytic reaction, CeO_2 can be release and storage oxygen on the basis of different reaction conditions, CeO_2 in the lean oxygen atmosphere can release oxygen and produce oxygen vacancy, and the oxygen vacancy in oxygen-enriched environment can be restored again, therefore, improving the oxygen storage of the material has a very important impact on its catalytic performance. Guo and Liu [18,19] reported that high CO conversion could be achieved over a Co_3O_4–CeO_2 catalyst. The addition of MnO_x could promote the interaction between Co_3O_4 and CeO_2, and thus increase the Co^{3+} content in the catalyst, which may enhance the selectivity for CO oxidation. Kang et al. [11] compared the catalytic activity of various metal oxides for CO oxidation and found that CoO_x/CeO_2 was most superior among the CeO_2 supported CoO_x, CuO, MnO_2, NiO, Cr_2O_3, Fe_2O_3 and V_2O_5 catalysts.

Preparation method affects the physicochemical and catalytic properties of the catalysts. Several methods such as co-precipitation and the impregnation method have been used for the catalyst preparation. The combustion method is one of the attractive techniques for catalyst synthesis due to its simplicity and the productivity. The resulting materials usually are homogeneous with nanocrystalline powders since the combustion reaction is vigorous and reaches high temperatures. This method have been applied for the methanol synthesis [20], solid oxide fuel cells [21], and supercapacitor application [22]. Avgouropoulos et al. [23] synthesized CuO–CeO_2 catalysts via the urea-nitrate combustion, which remained very active and stable, remarkably selective and with good tolerance towards CO_2 and H_2O, and compared co-precipitation, the citrate-hydrothermal, the urea-nitrates combustion, and the impregnation preparation method on the physicochemical and catalytic properties of CuO–CeO_2 catalysts for the selective CO oxidation in simulated reformate gas, it shown that the combustion-prepared sample exhibited the best catalytic performance [24]. Glycine-nitrate combustion synthesis is a promising combustion method for the preparation of metal oxide powders since higher combustion heat of glycine than urea could favor the combination of different metallic element [25,26].

In this study, the Co/CeO_2 prepared by combustion method are expected to be used as efficient catalysts for the CO-PrOx. However, to the best of our knowledge, there is few study on the CO-PrOx over Co/CeO_2 prepared by a glycine-nitrate combustion method. A series Co/CeO_2 catalyst have been synthesized and tested for the CO-PrOx.

2. Experimental

2.1. *Preparation of Co/CeO_2 catalysts*

Co/CeO_2 catalysts with different Co/Ce molar ratios were prepared by the glycine-nitrate combustion method. The Co/Ce molar ratios can be calculated as below,

$$\mathrm{Co/Ce} = 3\frac{x\cdot m_{\mathrm{total}}}{M_{\mathrm{Co_3O_4}}}\Big/\frac{(100-x)\cdot m_{\mathrm{total}}}{M_{\mathrm{CeO_2}}}$$

x, represent the mass fraction.

The requisite quantities of Analytic-grade $Co(NO_3)_2\cdot 6H_2O$ and $Ce(NO_3)_3\cdot 6H_2O$ were mixed in the appropriate molar ratios with a minimum volume of distilled water to form a transparent solution. Then the glycine solution was slowly added to the metal nitrate aqueous solution under constant stirring. The initial glycine/nitrate molar ratio was adjusted according to the principle of propellant chemistry [27]. The glycine to nitrate ratio was set to 0.3 as the literature described [28]. The resulting solution was placed in an ultrasound bath operating at 47 kHz with power of 45 W for half an hour in order to gain transparent sol. Afterwards, the crucible was dried at 80 °C in an oven until a transparent moisture-sensitive glassy material was obtained. This glassy material covered by the fine-mesh sieve was heated in an muffle furnace up to around 190 °C, which resulted spontaneous combustion with the evolution of large amounts of gases and a foamy voluminous powder then the powder was heated at 500 °C for 1 h to burn off any carbonaceous residues on the catalyst.

2.2. *Catalyst characterization*

The specific surface area, the pore volume and the pore size distribution of the sample were determined from the adsorption and desorption isotherms of nitrogen at −196 °C after outgassing procedure under vacuum at 300 °C for 10 h, using a Quantachrome Autosorb-1 instrument. X-ray diffraction (XRD) analysis was performed in the PANalytical X'Pert diffractometer (X'Pert PRO MPD, PW3040/60) within the 2-θ ranged from 10° to 90° by a speed of 6° per minute with Cu-Kα ($\lambda = 0.154060$ nm) radiation (40 kV, 40 mA). The crystallite size was calculated by the Scherrer equation from the XRD spectra. The surface morphology was observed by the Field emission-scanning electron microscope (FE-SEM, S-4800). Raman spectra were obtained by using a HORIBA JOBIN YVON LabRAM HR 800 system with a 632.81 nm laser source. Temperature-programmed reduction (TPR) was carried out by using 10 vol.% H_2/N_2 as a reducing gas in a linear quartz