



Effect of the well-designed functional groups and defects of porous carbon spheres on the catalytic oxidation performance



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ABSTRACT

The oxygen functional groups and defects of carbon material played an important role in dispersion of active components and additives, reduction of Ce⁴⁺, etc. The reduction of Ce⁴⁺ and structure defects would increase surface oxygen concentration and oxygen vacancies. The dispersion of active components and additives, surface oxygen concentration and structure defects were key factor on CO oxidation. The oxygen functional groups and structure defects of porous carbon spheres (PCSs) increased by O₃ treatment method. The effects of O₃ treatment concentration on structures, properties of PCSs support and Pd-Ce/PCSs were investigated in detail. The particle size of PCSs had not been changed basically after O₃ treatment. However, the outer of PCSs became uneven, which was main reason of the external surface area increase. The content of surface Pd⁴⁺, surface adsorption oxygen concentration, oxygen vacancies, defects, increased with increasing O₃ treatment concentration. Relationship between the functional groups, defects of porous carbon spheres and their catalytic performance was investigated in detail. CO oxidation test showed that the Pd-Ce based catalysts supported by the PCSs after O₃ treatment concentration for 45 mgL⁻¹ had the best activity. The effect of moisture on CO conversion was explored, and the catalysts showed excellent stability under moisture condition.

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1. Introduction

The oxidation of carbon monoxide is of great practical importance and is, for example, one of the main reactions in commercial three-way-catalysts (TWC) that are employed to control automotive emissions [1–4]. Palladium represents a major constituent of the CO oxidation catalyst and it is well-known that the catalytic properties of the noble metal strongly depend on electrons deliver, dispersion of active component and promoter, interaction of metal-support [5,6]. However, the surface properties of supports have an important role in the catalytic properties of the noble metal catalysts because it decides the anchoring and dispersion of active component and promoter, electrons deliver, interaction of metal-support [7,8]. Therefore, the research of support properties is must be in field of improving the catalysts activity.

As same as activated carbon, the porous carbon spheres (PCSs) possess high specific surface area, various porous structures, high resistance to acid and basic environment, good mechanical

stability, convenient synthetic procedure and low cost [9–11]. Besides, the structure controllable adjustment, abundant functional groups containing oxygen and structure defects of porous carbon spheres make it wider application in many fields, such as adsorbent, catalyst support and catalyst, etc. Subsequently, carbon-based catalysts [12–14] possess great potential due to their high the oxygen reduction reaction (ORR) activity, long-term stability, and low cost. Furthermore, the ORR performance of carbon-based catalysts can be significantly enhanced through doping with the active functional groups containing oxygen and structure defects. Carbon with O₃ treatment in air could increase the surface concentration of the active functional groups containing oxygen and defect sites. The performance, structure, dispersivity and morphology of the catalysts are influenced by the surface concentration of the active functional groups containing oxygen, defect sites [15]. Besides, these surface functional groups and defect sites on carbon material play an important role in the dispersion of active constituent and reduction of Ce⁴⁺ [16–18]. Du et al. [16] synthesized palladium-doped ceria and carbon core-sheath nanowire network (Pd-CeO₂@C CSNWN), the Pd-CeO₂@C contain much more Ce³⁺ than Pd-CeO₂, more Ce³⁺ ions mean higher concentration of oxygen

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vacancies, which leads to the release of more oxygen-containing species, thus promoting the oxidation of C₂H₅OH on the surface of Pd. Kim et al. [17] resulted in the formation of mesoporous ceria-carbon via a facile evaporation-induced self-assembly method, the constructed meso-CeO₂/C exhibited higher resolution in electrochemical detection of H₂O₂ than pure mesoporous carbon without ceria owing to the catalytic activity of ceria, this was because the oxygen functional groups and structure defects of carbon material played an important role in dispersion of active components and additives, reduction of Ce⁴⁺, making target glucose was rapidly converted into hydroxyl radicals by the catalytic activity of CeO₂. In summary, the oxygen functional groups and structure defects of carbon material is a method to increase activity Pd-Ce based catalysts.

In this paper, PCSs had been prepared by the surfactant assisted-hydrothermal method and the oxygen functional groups and defect sites of PCSs were well adjusted by O₃ treatment. The O₃ treated PCSs were used as a support for the catalyst. The effect of O₃ concentration on catalysts performance was studied in detail.

2. Experimental

2.1. Synthesis of PCSs

According to literature [19], PCSs were synthesized by surfactant assisted-hydrothermal method. Taken a certain glucose and polyvinylpyrrolidone were dissolved in 80 mL distilled water. Then the mix solution was transferred into a 100 mL teflon-lined stainless steel autoclave, and hydrothermally treated in a vacuum oven at 180 °C for 7 h. After cooling down naturally, the black precipitate was collected and sequentially washed with water and anhydrous ethanol. Then the precipitate was dried at 80 °C for 6 h, and calcined at 750 °C for 2 h (2 °C min⁻¹).

2.2. Carbon support pretreatment

PCSs was weighed and put smoothly in quartz tube with a diameter of 2 cm. Then they were treated by O₃ at a temperature of 100 °C for 15 min, respectively. The O₃ concentration was adjusted to 45 mgL⁻¹, 30 mgL⁻¹, 15 mgL⁻¹ and 0 mgL⁻¹ respectively. The treated PCSs were transferred into a vacuum vessel for storage. The obtained brown solid was identified as PCSs-x, x was the concentration of O₃ treatment.

2.3. Preparation of catalyst

The Pd-Ce/PCSs-x catalyst was prepared by impregnation method. Typically, an aqueous solution of Pd(NO₃)₂ and Ce(NO₃)₃ was added dropwise to PCSs-x, and then impregnated for 4 h. The Pd Loading amount was 1.0 wt.%. Ce loading was 5.0 wt%. The final catalysts were dried at 60 °C for 12 h and calcined at 200 °C for 5 h (5 °C min⁻¹).

2.4. Catalyst characterization

Powder X-ray diffraction (XRD) analysis was performed to verify the crystallographic phases present in supports and catalysts. XRD patterns of the samples were recorded on a Rigaku D/MAX-RB X-ray diffractometer with a target of Cu K α operated at 60 kV and 55 mA. XRD patterns were recorded in the 2 θ ranged of 20–80° with a scanning speed of 0.5°/min. Chemical states of the atoms in the catalyst surface were investigated by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 210 Electron Spectrometer (Mg K α radiation; h ν = 1253.6 eV). XPS data were calibrated using the binding energy of C1s (284.6 eV) as the standard. Transmission

electron microscopy (TEM) experiments were carried out to study the fine morphology of the carbon material, using a FEI TECNAIG² Microscope operated at 200 kV. Raman spectra were taken under ambient conditions by using a RM 2000 microscope confocal Raman spectrometer (Renishaw PLC) using 514 nm laser. The specific surface areas were calculated by using the Brunauer-Emmett-Teller (BET) model, with a Micromeritics ASAP 2010 instrument. The pore size distributions were obtained using the adsorption branch of the nitrogen isotherms by applying the Barrett-Joyner-Halenda (BJH) method. Prior to measurements, the samples were degassed at 150 °C for 6 h.

2.5. Measurements of catalytic performance

Catalytic activity tests were performed in a continuous-flow fixed-bed microreactor. A glass tube with an inner diameter of 6 mm was chosen as the reactor tube. About 300 mg catalyst with the average diameter of 20–40 mesh was placed into the tube. The reaction gas mixture consisting of 1.0 vol.% CO balanced with air was passed through the catalyst bed at a total flow rate of 50 ml min⁻¹. A typical weigh hourly space velocity (WHSV) was 10000 mL g⁻¹ h⁻¹. The composition of the influent and effluent gas was detected with an online GC-7890II gas chromatograph equipped with a thermal conductivity detector and a molecular sieve 5A column. As we all know, CO oxidation reaction is accompanied by a reduction in the number of moles. In this paper, this change of moles was neglected. Therefore, the CO conversion rate (X_{CO}) was calculated:

$$X_{\text{CO}} = \frac{([\text{CO}]_{\text{in}} \text{vol.}\% - [\text{CO}]_{\text{out}} \text{vol.}\%)}{[\text{CO}]_{\text{in}} \text{vol.}\%} \times 100$$

3. Results and discussion

Porous carbon spheres (PCSs) acts as the pathway of electrons transport and a support for activated groups of the catalyst. The structure and performance of catalysts are influenced mainly by specific surface area, porosity of the support, defect sites and the functional groups on it [20]. The chemical or physical treatments of carbon support can be used to change these properties. The performance of catalysts can be affected remarkably by these properties. Therefore, the PCSs support and Pd-Ce/PCSs catalysts were characterization by BET, XRD, Raman and XPS, etc.

3.1. Support characterization

Fig. 1 shows the proposed formation process of PCSs and modified PCSs. The PCSs were synthesized by surfactant assisted hydrothermal method, the PCSs-0 possessed uniform sizes and smooth outer surfaces. After O₃ treatment, modified PCSs were kept constant particle size and morphology. However, the outer surfaces of carbon spheres became uneven.

The structural differences of PCSs-0, PCSs-15, PCSs-30 and PCSs-45 are further demonstrated by N₂ adsorption-desorption isotherms (Fig. 2). The branches of adsorption and desorption of all isotherms parallel to each other at the relative pressure range of 0.2–0.8. All isotherms exhibited type IV isotherms with H₄ hysteresis loop (IUPAC classification), indicating that PCSs existed micropores and mesoporous structure. The data derived from adsorption-desorption isotherms of PCSs treatment by O₃ at different time and same temperature in Fig. 1 are listed in Table 1.

Table 1 summarizes BET specific surface areas, external surface area, pore volumes of PCSs treatment by O₃ at different

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