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Synthesis of Pd nanoparticles supported on CeO_2 nanotubes for CO oxidation at low temperatures

Jingmi Wu [a], Liang Zeng [b], Dangguo Cheng [a,*], Fengqiu Chen [a], Xiaoli Zhan [a], Jinlong Gong [b,#]

[a] *Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, Zhejiang, China*

[b] *Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University; Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China*

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ABSTRACT

Developing efficient supported Pd catalysts and understanding their catalytic mechanism in CO oxidation are challenging research topics in recent years. This paper describes the synthesis of Pd nanoparticles supported on CeO_2 nanotubes via an alcohol reduction method. The effect of the support morphology on the catalytic reaction was explored. Subsequently, the performance of the prepared catalysts was investigated toward CO oxidation reaction and characterized by Nitrogen sorption, X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and CO-temperature-programmed desorption techniques. The results indicated that the catalyst of Pd on CeO_2 nanotubes exhibits excellent activity in CO oxidation at low temperatures, due to its large surface area, the high dispersion of Pd species, the mesoporous and tubular structure of the CeO_2-nanotube support, the abundant Ce^{3+}, formation of Pd–O–Ce bonding, and enhanced metal–support interaction on the catalyst surface.

1. Introduction

The low temperature oxidation of carbon monoxide (CO) has gained much attention owing to its numerous applications such as in CO gas sensors [1] and automobile exhaust purification [2]. Supported noble metals (e.g., Ag, Au, Pd, Pt) have been considered as efficient catalysts for CO oxidation processes [3–7]. Among them, supported Pd catalysts are considered to be promising owing to their excellent activity. Though Ag and Au catalysts can convert CO at room temperature or below, the melting points of Ag (960 °C) and Au (1063 °C) are lower than that of Pd (1550 °C). Consequently, Ag and Au nanoparticles are more prone to sintering during the process, thereby lowering the performance of the catalyst. Similar to Pd catalysts, Pt catalysts feature a high melting point (1769 °C); however, Pt supported catalysts are more expensive than Pd catalysts.

Much effort has been devoted in understanding the catalytic oxidation of CO over Pd catalysts. Currently, it is widely believed that this reaction follows a Langmuir-Hinshelwood mechanism, involving the reaction between CO adsorbed onto the Pd species and oxygen from ceria at the metal-ceria interface [8]. However, to date, the nature of the active species for

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* Corresponding author. Tel: +86-571-87953382; Fax: +86-571-87951227; E-mail: dgcheng@zju.edu.cn
# Corresponding author. Tel/Fax: +86-22-87401818; E-mail: jlgong@tju.edu.cn

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this reaction remains unclear and a challenging research topic. For example, both Pd and PdO species were identified as the active sites for CO oxidation by Venezia [9]. Other research studies reported that the enhanced performance of Pd supported on CeO_2 catalyst could be due to the ionic dispersion of Pd on CeO_2 that leads to a strong metal-ceria interaction [10]. Furthermore, as demonstrated, the high dispersion of active species promotes the reaction over Pd catalysts [11].

Additionally, the morphology, exposed crystal facets, oxygen vacancies, and pore structure of CeO_2 play vital roles in determining the catalyst activity. Various CeO_2 nanostructures, such as nanorods, nanowires, and nanocubes, were recently synthesized and investigated as supports in CO oxidation [12]. The results demonstrated that the catalyst activity toward CO oxidation was greatly dependent on the shape of CeO_2. Yuan and his co-workers [13] prepared a series of Au supported on CeO_2 catalysts, and experimentally observed that CeO_2 nanorods featured a considerably higher oxygen storage capacity and exhibited superior activity toward CO oxidation when compared with CeO_2 nanocubes. Furthermore, it was found that the preferentially exposed crystal planes (100) and (110) of CeO_2 nanorods were more active toward CO oxidation than the crystal plane (111) of the corresponding nanoparticles [14]. Zhu [15] showed that the catalytic activity of Pd supported on CeO_2 catalysts could be improved by employing a pre-reduction treatment, particularly a low-temperature reduction pre-treatment, which promotes oxygen vacancy formation and enhances metal-support interactions. This interaction was also considered by many other researchers as discussed. As reported, cationic Pd species were formed owing to the strong interaction between Pd and CeO_2 [16,17], and accordingly Pd^{2+} ions in the CeO_2 matrix were suggested as the active sites of the low-temperature oxidation of CO [18]. In another study, Tang [19] examined the effect of the pore structure of CeO_2 on CO oxidation; three types of CeO_2 nanomaterials with different pore structures were synthesized i.e., mesoporous, microporous, and nanoparticle CeO_2. The results showed that Pd supported on mesoporous CeO_2 exhibited the highest catalytic activity among the prepared catalysts. The superior activity was ascribed to the mesoporous structure, large surface area, and abundant surface oxygen species of the mesoporous CeO_2 support.

Based on the above analyses, CeO_2 nanotubes could be considered as potential supports for CO oxidation owing to their advantageous properties such as high surface area and tubular morphology [20]. Thus, in this work, we prepared CeO_2 nanotube-supported Pd catalysts for application in CO oxidation at low temperatures. To achieve a high dispersion of metal particles, a novel alcohol reduction method [21,22] was used to stabilize the Pd nanoparticles on the support. A series of catalysts with different Pd contents were prepared and characterized by Nitrogen sorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and CO-temperature-programmed desorption (CO-TPD) techniques. The relationship between the structure and activity of the catalysts was explored to contribute to ongoing discussion regarding the role of active Pd species in CO oxidation.

2. Experimental

2.1. *Materials preparation*

CeO_2 nanotubes were prepared by the hydrothermal method using poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEO-PPO-PEO; P123) as the surfactant [23].

Poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilized Pd nanoparticles (NPs) were synthesized using an alcohol reduction method. First, H_2PdCl_4 aqueous solution (2.0 mmol/L) was prepared by dissolving the precursor $PdCl_2$ solution (Sinopharm Chemical Reagent Co., Ltd.) in HCl aqueous solution. Then, in a typical synthesis, H_2PdCl_4 aqueous solution (45 mL), ethanol (60 mL), H_2O (40 mL), and PVP (0.4 g) were refluxed at 90 °C for 3 h. The as-prepared Pd NPs were collected by vacuum rotary evaporation and then re-dispersed and stored in ethanol (40 mL).

For the preparation of Pd supported on CeO_2 nanotubes (Pd/CeO_2-nanotube), the following procedure was employed. CeO_2 nanotubes (1 g) were added to a required amount of the above Pd NPs ethanolic solution. The mixture was stirred for 24 h to obtain a homogeneous suspension. Then, the suspension was evaporated in a rotary evaporator under vacuum conditions and dried in an oven at 110 °C, followed by calcination at 500 °C in air for 2 h. Three Pd/CeO_2-nanotube catalysts with varying Pd contents of 0.3, 0.6, and 0.9 wt% were prepared, and are referred as 0.3Pd/CeO_2-nanotube, 0.6Pd/CeO_2-nanotube, 0.9Pd/CeO_2-nanotube, respectively. Additionally, for comparison, commercial CeO_2 (Sinopharm Chemical Reagent Co., Ltd.) was used as a support to prepare Pd supported on CeO_2 with a Pd content of 0.9 wt%, and referred as 0.9Pd/CeO_2. The same preparation procedure as that used for preparing Pd/CeO_2-nanotube materials was employed.

2.2. *Catalytic test*

The catalytic activity tests were performed in a continuous flow fixed bed reactor. A stainless steel tube with an inner diameter of 8 mm was used as the reactor. The catalyst (100 mg) with a diameter of 20–40 mesh was introduced into the reactor. The reaction gas mixture consisting of CO (1 vol%), O_2 (4 vol%), and He (95 vol%) was passed through the catalyst bed at a total flow rate of 20 mL/min. The composition of the influent and effluent gases was determined using an online GC-9860 gas chromatograph equipped with a thermal conductivity detector. The CO conversion was evaluated based on the CO concentration difference between the inlet and outlet.

2.3. *Catalyst characterization*

Nitrogen sorption analysis was performed on a Micromeritics ASAP 2020 to determine the BET specific surface area and BJH pore diameter distribution of the samples. Powder X-ray diffraction (XRD) was performed on a Shimadzu XRD-6000 to identify the crystallographic phase of the samples. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical states of the atoms on the sample surface, as performed on a