



Boundary role of Nano-Pd catalyst supported on ceria and the approach of promoting the boundary effect



Gaigai Si^a, Jun Yu^{a,*}, Xiuzhen Xiao^a, Xiaoming Guo^a, Houjin Huang^a, Dongsen Mao^a, Guanzhong Lu^{a,b,**}

^a Research Institute of Applied Catalysis, School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China

^b Key Laboratory for Advanced Materials and Research Institute of Industrial catalysis, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

Recently, the interface catalysis has caused more and more attentions. Herein, we developed an approach to strengthen the boundary role of Pd/CeO₂ catalyst, resulting in an obvious increase in its catalytic performance for CO oxidation

with 100% CO conversion at 20 °C. The results show that after the pretreatment in N₂ at 750 °C and reduction in H₂ at 300 °C, the interaction between Pd and CeO₂ was enhanced, and smaller Pd⁰ particles and longer interface length (*l*₀) of Pd-CeO₂ were obtained. In the boundary of Pd-CeO₂, the presence of Pd²⁺ promotes the formation of oxygen vacancies in CeO₂, and CO adsorbed on Pd⁰ reacts with the oxygen species activated by the oxygen vacancy. The Pd⁰ sites and oxygen vacancies in the boundary play a decisive role in the CO oxidation over Pd/CeO₂, which is proved by the B-TOF and I₀ × B-TOF.

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1. Introduction

The Pd/CeO₂ catalysts for low-temperature CO oxidation were widely studied in recent years, because of their outstanding activity and stability [1–6]. When CeO₂ was used as a support of precious metals, the metal-support interaction would induce the synergistic oxidation/reduction of both the metal and support, resulting in an increase in their catalytic performances in wide applications, especially for CO oxidation [1–3]. Concerning the reaction mechanism for CO oxidation over supported catalyst, it is generally believed that the reaction takes place at the metal-support interface [7], thus the interfacial effect has attracted much attention in recent years.

Many researchers have investigated the effect of the palladium loading on the catalytic activity of Pd/CeO₂ [8,9]. The results show that the catalytic activity is connected with the Pd loading, but it is not the only relevant factor, because there is a perfect content in the certain conditions rather than the activity is certainly increased with the increasing of Pd content. The geometric structures of ceria support and the synergy between the Pd species and ceria also play

an important role in CO oxidation [4,9–12]. To improve the interaction between Pd and ceria and further enhance their synergy effects, a lot of methods have been applied. (1) The appropriate preparation methods were adopted. Li et al. [8,9] prepared Pd/CeO₂ catalyst by improving protocol and one-pot co-precipitation method, and showed that the catalysts exhibited the promising activity for low-temperature CO oxidation. Using the solution-combustion method, the PdO/Ce_{1-x}Pd_xO_{2-δ} catalyst containing free surface PdO species and PdO species in Ce_{1-x}Pd_xO_{2-δ} solid solution was obtained, and the synergetic effects of surface free PdO species and Ce_{1-x}Pd_xO_{2-δ} solid solution led to facile reaction of CO and O₂ [7,13]. The hollow Pd-CeO₂ nanocomposite spheres and cage-bell Pd@CeO₂ nanoparticle aggregates were prepared by means of template synthesis, in which Pd was highly dispersed in the catalysts, so that there is larger Pd-CeO₂ interface [10,14], resulting in the higher catalytic activity for low-temperature oxidation of CO. Besides, other preparation methods such as pulsed laser ablation, plasma-arc, sol-gel precipitation and microemulsion were also used [11,15–17]. (2) Utilizing the exposed crystal facets of CeO₂ with different morphologies regulates and controls the interactions with the supported Pd species [18–22]. For instance, we described that the structure and chemical state of Pd supported on ceria were affected by ceria facets, thus influencing its catalytic activity [4]. (3) Treatment with different atmosphere and temperatures was used to improve the interaction between Pd and ceria [1,3,5,10,11,23]. Hinokuma et al. [1] found

* Corresponding author.

** Corresponding author at: Research Institute of Applied Catalysis, School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China.

E-mail addresses: yujun@sit.edu.cn (J. Yu), gzhlu@ecust.edu.cn (G. Lu).

that after Pd/CeO₂ was aged at 900 °C in air, its catalytic activity increased by more than 20 times for ambient-temperature CO oxidation, despite of a significant sintering and loss of the surface area from 92 to 7 m²/g. Some researchers utilized XPS and other analysis methods to investigate the state of Pd species and the interaction between Pd and ceria, certifying that the perfect interaction could be obtained at certain temperature and in the atmosphere of oxygen [12,23]. Wang et al. [3] treated the catalysts in static air and H₂/O₂ alternating flow at 800 °C respectively, and found that the catalytic activity of the redox treated catalyst was seriously weakened compared with the oxidative-treated one, due to the encapsulation of Pd crystallites by the CeO₂ support during the redox treatment.

In this paper, we focused on the study of the role of boundary or interface catalysis in the Pd/CeO₂ catalyst, and how to enhance the role of boundary between Pd and ceria phases by the treatment in flowing N₂ gas at different temperatures, followed by reduction in H₂. This results in a stronger interaction between Pd and ceria and higher dispersion of Pd species on ceria, which improves its catalytic activity and stability for CO oxidation remarkably.

2. Experimental

2.1. Catalyst preparation

PdCl₂ (AR) and Ce(NO₃)₃·6H₂O (AR) was purchased from Shanghai Titanchem Co., Ltd. CeO₂ was obtained by direct calcination of Ce(NO₃)₃·6H₂O in static air at 350 °C for 2 h. The Pd/CeO₂ catalysts with different Pd loadings were prepared by the incipient-wetness impregnation method. The calculated amount of PdCl₂ was dissolved in 2 mL solution of 0.1 M HCl, and then 2 g prepared CeO₂ was added in the PdCl₂ solution under ultrasonic treatment for 1 min and dried at 60 °C overnight. Before characterization and catalytic activity testing, the catalysts were thermally treated in the flowing N₂ for 2 h and reduced in H₂ for 1 h online. In the “catalyst-T/N-T/H” sample, T is the treatment temperature (°C), and N or H indicates the N₂ (99.999%) or 10% H₂/N₂ gas.

2.2. Evaluation of the catalytic activity

The catalytic activity of the catalyst for CO oxidation was tested in a fixed bed quartz tubular reactor (ID = 4 mm) with 200 mg catalyst after 10 min of steady operation. Before testing activity, the catalyst was treated at 500–800 °C in N₂ (20 mL/min) for 2 h and reduced in 10% H₂/N₂ at 300 °C for 1 h (20 mL/min). The reactant gas was consisted of 0.15% CO/Air (50 mL/min) and the space velocity was 15000 mL/(h·g_{cat}). When the catalytic activity was tested in the presence of moisture, the reactant gas passed through a water vapor saturator, and varying the temperature of the saturator could adjust the water concentration in the reactant gas. The CO concentration was analyzed online by a gas chromatograph (GC 2060) equipped with a hydrogen flame ionization detector (FID), in which a methanizer was used for hydrogenating CO and CO₂ to methane. The CO conversion (X_{CO}) was calculated by X_{CO} (%) = ([CO]_{in} - [CO]_{out})/[CO]_{in} × 100, where [CO]_{in} and [CO]_{out} are the CO concentration of the inlet and outlet gas, respectively.

The turnover frequency (TOF) was calculated by TOF = (X_{CO}·V_{CO}·N_A)/N_α [4]. And the boundary-turnover frequency (B-TOF) of the CO oxidation was used to indicate the catalyst activity, which means the molecule number of CO oxidized per second per Pd⁰ atom in the boundary between Pd particle and CeO₂. That is to say, B-TOF was calculated on the Pd sites in the boundary rather than on all Pd sites on the whole surface. We assumed that the Pd particle is hemispherical and the Pd-Ce interface is the circle geometry [4,24–26], thus B-TOF

is calculated by B-TOF = (X_{CO}·V_{CO}·N_A)/N_β [26], where X_{CO} is the CO conversion, V_{CO} is the CO gas flow rate (mol/s), N_A is the Avogadro constant and N_α is the number of catalytically active sites (N_α = N_t·D_{Pd}) on the surface, N_t is the total amount of Pd atoms, N_β is the Pd⁰ atoms in the boundary between Pd particle and CeO₂ (N_β = V_{Pd}/(0.5 × (4/3)π·(d/2)³) × (πd/2r) = 6V_{Pd}/(d² × r)), V_{Pd} is the total volume of Pd particles (V_{Pd} = N_t·((4/3)π·r³)), d is Pd average particle diameter (d = 1.12/D_{Pd}) [4], r is the radius of the Pd atom, which is 0.137 nm [27]. The total length of the perimeter of the Pd–Ce interface (I₀) was also calculated (I₀ = N_β × 2r). TON = B-TOF·N_α × TOF = N_β × B-TOF. The specific kinetic rate r_{CO}/I₀ (mol/(m·s)) based on the length of Pd–CeO₂ interface I₀ was calculated by r_{CO}/I₀ = (X_{CO}·V_{CO})/I₀ [24,25].

The Pd dispersion (D_{Pd}) was measured by H₂-O₂ titration [28–31], the catalyst was oxidized in air (20% O₂/N₂, 20 mL/min) at 300 °C for 1 h, and then it was cooled down to 120 °C and He (20 mL/min) was swept the catalyst bed for 30 min to eliminate the physically adsorbed O₂. Subsequently, H₂ pulse was introduced to the sample. Based on the reaction stoichiometry of Pd + 1/2O₂ → PdO and PdO + 3/2H₂ → PdH + H₂O, D_{Pd} was calculated by D_{Pd} = N_α/N_t = ((2/3)·V₀·M·N_A)/(22400N_A·WP) = 3.167 × 10⁻³ × V₀/(W·P), where V₀ is the adsorption volume of hydrogen (mL), W is the weight of the sample (g), P is the mass percentage of Pd in the sample (wt.%), and M is the molar mass of Pd (106.4 g/mol).

2.3. Catalyst characterization

The Pd content in the catalyst was obtained by an inductively coupled plasma optical emission spectrometry (ICP-OES) on a PerkinElmer Optima 7000 DV instrument. The X-ray powder diffraction (XRD) patterns of the catalysts were tested on a PANalytical X'Pert Pro MRD X-ray diffractometer with CuKα radiation (λ = 0.154056 nm) operated at 40 kV and 40 mA. The surface areas of the samples were measured by N₂ adsorption at -196 °C on a Micrometrics ASAP 2020 M + C adsorption apparatus. The transmission electron microscopy (TEM) images were taken on a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI Corporation) operated at 200 kV.

In situ XPS spectra were obtained on a Thermo Scientific ESCALAB 250Xi, and survey spectra were recorded with the pass energy of 160 eV, and high resolution spectra with the pass energy of 30 eV. The base vacuum during XPS analysis was greater than 10⁻⁶ kPa. The binding energies (BE) were calibrated with the C 1s line (284.6 eV) originating from carbon. All the samples were treated online. For the Pd/CeO₂ sample, it was treated in N₂ (20 mL/min) at 750 °C for 1 h, and after cooling down to 30 °C in N₂ in the reaction chamber, the sample was transferred to the analysis chamber by a transfer rod under ultra-high vacuum, then the XPS spectra of Pd/CeO₂-750/N were taken. After that, this sample was moved to the reaction chamber and reduced in 10% H₂/N₂ (20 mL/min) at 300 °C for 1 h, and after cooling down to 30 °C in 10% H₂/N₂, the sample was transferred to the analysis chamber, then the XPS spectra of Pd/CeO₂-750/N-300/H was obtained. After the Pd/CeO₂-750/N-300/H catalyst was treated in the reaction chamber in the gas of 1.5% CO/N₂ (5 mL/min) at 30 °C for 30 min, the sample was moved to the analysis chamber, and then the XPS spectra of CO adsorbed on the Pd/CeO₂-750/N-300/H catalyst were obtained. When the reactant gas of 0.15% CO/Air (50 mL/min) was used instead of 1.5% CO/N₂ (5 mL/min), the *in situ* XPS spectra of the Pd/CeO₂-750/N-300/H catalyst after the surface reaction of CO oxidation were obtained. The nonlinear curve-fitting process of Pd 3d, Ce 3d and O 1s was performed by the XPSPEAK 4.1 software package with a Shirley background and a convolution of Lorentzian-Gaussian functions (80/20).

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