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# Three-dimensionally ordered macroporous $CeO_2$-supported Pd@Co nanoparticles: Highly active catalysts for methane oxidation

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ABSTRACT

Three-dimensionally ordered macroporous $CeO_2$ (3DOM $CeO_2$) and its supported Pd@Co ($Co_xPd$/3DOM $CeO_2$, $x$ (Co/Pd molar ratio) = 2.4–13.6) nanocatalysts were prepared using the polymethyl methacrylate-templating and modified polyvinyl alcohol-protected reduction methods, respectively. The Pd@Co particles displayed a core-shell (core: Pd; shell: Co) structure with an average size of 3.5–4.5 nm and were well dispersed on the surface of 3DOM $CeO_2$. The $Co_xPd$/3DOM $CeO_2$ samples exhibited high catalytic performance and super stability for methane oxidation, with the $Co_{3.5}Pd$/3DOM $CeO_2$ sample showing the highest activity ($T_{90\%}$ = 480 °C at space velocity of 40,000 mL/(g h) and excellent stability in the temperature range 400–800 °C. The apparent activation energies (58–73 kJ/mol) obtained over $Co_xPd$/3DOM $CeO_2$ were much lower than those (104–112 kJ/mol) over Co/3DOM $CeO_2$ and 3DOM $CeO_2$ for methane oxidation, with the $Co_{3.5}Pd$/3DOM $CeO_2$ sample possessing the lowest apparent activation energy (58 kJ/mol). It is concluded that the excellent catalytic performance of $Co_{3.5}Pd$/3DOM $CeO_2$ was associated with its good abilities to adsorb oxygen and methane as well as the unique core-shell structure of CoPd nanoparticles.

## 1. Introduction

As a main component of natural gas, methane ($CH_4$) is a greenhouse gas that has a huge global warming potential, as high as that of $CO_2$ in the past 20 years. Therefore, more and more attention has been paid to reducing the emission of $CH_4$ from industrial and transportation activities, which would give rise to substantial environmental and economic benefits. Catalytic oxidation of $CH_4$ at low temperatures over precious metal (e.g., Pd-, Rh-, or Pt)-based catalysts is a potential practical technology. Supported palladium shows high catalytic activity for methane oxidation and is commonly used in a number of catalysts [1,2]. However, reducing the high cost and enhancing the stability at high temperatures of a catalyst are always hot topics.

Nowadays, many efforts to reduce the use of noble metals are mainly focused on the preparation of single-atom and base metal-promoted noble metal catalysts [2–8]. Because of their good stability, base metal-doped noble metal catalysts have gained much attention. For example, by introducing a certain amount of tin to palladium, Freakley and co-workers found that the obtained catalysts showed more than 95% $H_2O_2$ selectivity in the direct synthesis of $H_2O_2$ after sequential hydrogenation and decomposition reactions [8]. Sun and co-workers adopted a facile route to generate monodisperse MPd (M = Co, Cu) nanoparticles (NPs), and observed that the CoPd catalysts were highly efficient for the methanolysis of ammonia borane and the oxidation of formic acid [5,6]. Using a one-step seeding growth strategy, Yan et al. obtained Au@Co NPs that performed well in the hydrolytic dehydrogenation of ammonia borane [7]. The results of the above works demonstrate that Co is a good choice to modify the noble metal(s) and enhance their catalytic performance. As we know, a core–shell structure can provide a strong metal–support interaction by maximizing the interface, thus favoring improvement in activity [2,7]. In addition to improved performance, formation of a core–shell architecture can also minimize deactivation of the catalyst due to the sintering of metal(s) [9]. Catalyst deactivation is particularly pronounced in reactions involving high temperatures, especially $CH_4$ oxidation. It is envisioned that generating supported core-shell-structured Pd@Co NPs may meet the requirements for high catalytic activity and good stability in methane oxidation.

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Ceria is one of the most intensively investigated rare earth oxides. As a support, $CeO_2$ shows good ability to store and release oxygen and is beneficial for noble metal dispersion and metal–support interface formation [10,11]. Among a large number of Ce-based catalysts for methane oxidation, pure ceria exhibits fairly high catalytic activity [12,13]. Porous ceria with rich porosity, high surface area, narrow pore-size distribution, and good reducibility is expected to possess improved physicochemical properties. Due to good transportation and diffusion properties, three-dimensionally ordered macroporous (3DOM) catalysts have recently shown excellent activity for the oxidation of soot and volatile organic compounds (VOCs) [14–16]. Previously, our group adopted the polymethyl methacrylate (PMMA)-templating and polyvinyl alcohol (PVA)-protected reduction strategies to successfully generate a series of 3DOM-structured materials [16–19]. It was found that the 3DOM-structured gold-based nanomaterials performed excellently in the oxidation of CO or typical VOCs. Here, we report for the first time the preparation, characterization, and catalytic properties of 3DOM $CeO_2$-supported Pd@Co nanocatalysts (Pd@Co/3DOM $CeO_2$) for methane oxidation. Among the as-prepared samples, $Co_{3.5}Pd$/3DOM $CeO_2$ performed the best, which was associated with enhanced oxygen and methane adsorption ability and a unique Pd@Co core-shell structure.

## 2. Experimental

### 2.1. Catalyst preparation

Uniform monodisperse PMMA colloid crystal microspheres with an average diameter of ca. 300 nm were synthesized using a method described previously [20]. 3DOM $CeO_2$ was fabricated via the PMMA-templating route [10]. Typical fabrication procedures are as follows: 1.0 g of polyethylene glycol (PEG)-10000 and 4.34 g of $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in 10.0 g of ethanol aqueous solution (40 wt.%) under stirring. After dissolution, 2.0 g of the PMMA template was soaked in the above mixed solution for 4 h. After being filtered and dried at room temperature (RT) for 48 h, the obtained powders were calcined in a $N_2$ flow of 200 mL/min at a ramp of 1 °C/min from RT to 300 °C and kept at this temperature for 3 h, then cooled to 50 °C under the same atmosphere, and finally calcined in an air flow of 200 mL/min at a ramp of 1 °C/min from RT to 600 °C and maintained at this temperature for 5 h, thus generating the 3DOM $CeO_2$ support.

The Pd@Co NPs were synthesized using the modified PVA-protected reduction method with PVA ($MW_{aver.}$ = 10,000 g/mol) as protecting agent and $NaBH_4$ as reducing agent. The typical preparation procedures are as follows: A desired amount of PVA (noble metal/PVA mass ratio = 1.0:1.5) was added to an aqueous solution of $PdCl_2$ in an ice bath under stirring. Then a $NaBH_4$ aqueous solution (2.0 g/L; noble metal/$NaBH_4$ molar ratio = 1.0:5.0) was rapidly injected to form a dark brown suspension; after vigorous stirring for 5 min, a desired amount of $CoCl_2$ (1.5 mmol/L; the theoretical Co/Pd molar ratio ($x$) = 0, 3, 4, 8, and 14) was added to the mixed aqueous solution, thus obtaining the Pd@Co NPs after stirring for 1 h. The Pd NPs were synthesized using the same method in the absence of cobalt chloride.

The 3DOM $CeO_2$-supported Pd@Co or Pd samples were prepared using a gas-bubble-assisted adsorption strategy. A desired amount of the 3DOM support was added to the obtained Pd@Co or Pd suspension with a theoretical Pd@Co loading of 1.0 wt.% or Pd loading of 0.5 wt.%. This suspension was subjected to ultrasonic (60 kHz) treatment for 10 min. A gas-bubble-assisted adsorption operation with three outlets was adopted to make the reaction homogenous. After the suspension was bubbled with $N_2$ (100 mL/min) for 4 h, the wet solid was filtered, washed with 2.0 L of deionized water, dried at 80 °C for 12 h, and calcined in nitrogen flow at a ramp of 10 °C/min from RT to 600 °C and kept at 600 °C for 1 h, thus obtaining the supported Pd@Co or Pd samples. The results of inductively coupled plasma atomic emission spectroscopic (ICP–AES) investigations reveal that the real loading (0.71–0.93 wt.%) of Pd@Co was similar in each of the samples.

All of the chemicals (A.R. in purity) were purchased from the Beijing Chemical Reagents Company and used without further purification.

### 2.2. Catalyst characterization

Physicochemical properties of the 3DOM $CeO_2$ and CoPd/3DOM $CeO_2$ samples were characterized by ICP–AES, X-ray diffraction (XRD), $N_2$ adsorption–desorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-angle annular dark-field (HAADF–STEM), X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed reduction ($H_2$-TPR), oxygen temperature-programmed desorption ($O_2$-TPD), methane temperature-programmed desorption ($CH_4$-TPD), and in situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFT). The detailed characterization procedures are described in the Supplementary Material.

### 2.3. Catalytic activity evaluation

Catalytic activities of the samples were evaluated in a continuous-flow fixed-bed quartz tubular microreactor (i.d. 6.0 mm). To minimize the effect of hot spots, 50 mg of the sample (40–60 mesh) was diluted with 0.25 g of quartz sands (40–60 mesh). Before the test, each sample was treated in an oxygen flow of 30 mL/min at 300 °C for 1 h. The reactant mixture was composed of 2.5 vol% $CH_4$ + 20 vol% $O_2$ + 77.5 vol% $N_2$ (balance), and the total flow was 33.2 mL/min, thus giving a space velocity (SV) of ca. 40,000 mL/(g h). In the case of water vapor introduction, 5.0 vol% $H_2O$ was introduced by passing the feed stream through a water saturator at 34 °C. Reactants and products were analyzed online by gas chromatography (GC-14C, Shimadzu) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), using a Stabilwax column (30 m in length) for methane separation and a Carboxen 1000 column (3 m in length) for permanent gas detection. The balance of carbon throughout the catalytic system was estimated to be 99.5 ± 1.5%. Catalytic activities of the samples were evaluated using the temperatures required for achieving methane conversions of 10, 50, and 90%, respectively ($T_{10\%}$, $T_{50\%}$, and $T_{90\%}$). $CH_4$ conversion was defined as $(c_{\text{inlet}} - c_{\text{outlet}})/c_{\text{inlet}} \times 100\%$, where the $c_{\text{inlet}}$ and $c_{\text{outlet}}$ were the inlet and outlet $CH_4$ concentrations in the feed stream, respectively.

## 3. Results and discussion

### 3.1. Crystal phase composition, pore structure, and surface area

Fig. S1 of the Supplementary Material shows the XRD patterns of the 3DOM $CeO_2$ and $Co_xPd$/3DOM $CeO_2$ samples. According to the standard ceria sample (JCPDS PDF# 81-0792), the $CeO_2$ in 3DOM $CeO_2$ and $Co_xPd$/3DOM $CeO_2$ possessed a cubic crystal structure. No apparent diffraction peaks assignable to the Co and/or Pd phases were recorded due to their low loadings and good dispersion, suggesting that the loading of $Co_xPd$ NPs did not result in an obvious change in the crystal structure of $CeO_2$. According to the Scherrer equation ($D = 0.89\lambda/(\beta \cos\theta)$, where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum (FWHM) of the (1 1 1) plane of $CeO_2$, and $\theta$ is the corresponding diffraction angle), the grain sizes of $CeO_2$ in 3DOM $CeO_2$ and $Co_xPd$/3DOM $CeO_2$ were