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Synthesis of Pd nanoparticles supported on CeO₂ nanotubes for CO oxidation at low temperatures

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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 CeO₂ 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 CeO₂ 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 CeO₂-nanotube support, the abundant Ce³⁺, formation of Pd–O–Ce bonding, and enhanced metal-support interaction on the catalyst surface.

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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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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 CeO₂ catalyst could be due to the ionic dispersion of Pd on CeO₂ 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 CeO₂ play vital roles in determining the catalyst activity. Various CeO₂ 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 CeO₂. Yuan and his co-workers [13] prepared a series of Au supported on CeO₂ catalysts, and experimentally observed that CeO₂ nanorods featured a considerably higher oxygen storage capacity and exhibited superior activity toward CO oxidation when compared with CeO₂ nanocubes. Furthermore, it was found that the preferentially exposed crystal planes (100) and (110) of CeO₂ 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 CeO₂ 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 CeO₂ [16,17], and accordingly Pd²⁺ ions in the CeO₂ 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 CeO₂ on CO oxidation; three types of CeO₂ nanomaterials with different pore structures were synthesized i.e., mesoporous, microporous, and nanoparticle CeO₂. The results showed that Pd supported on mesoporous CeO₂ 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 CeO₂ support.

Based on the above analyses, CeO₂ 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 CeO₂ 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

CeO₂ 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, H₂PdCl₄ aqueous solution (2.0 mmol/L) was prepared by dissolving the precursor PdCl₂ solution (Sinopharm Chemical Reagent Co., Ltd.) in HCl aqueous solution. Then, in a typical synthesis, H₂PdCl₄ aqueous solution (45 mL), ethanol (60 mL), H₂O (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 CeO₂ nanotubes (Pd/CeO₂-nanotube), the following procedure was employed. CeO₂ 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/CeO₂-nanotube catalysts with varying Pd contents of 0.3, 0.6, and 0.9 wt% were prepared, and are referred as 0.3Pd/CeO₂-nanotube, 0.6Pd/CeO₂-nanotube, 0.9Pd/CeO₂-nanotube, respectively. Additionally, for comparison, commercial CeO₂ (Sinopharm Chemical Reagent Co., Ltd.) was used as a support to prepare Pd supported on CeO₂ with a Pd content of 0.9 wt%, and referred as 0.9Pd/CeO₂. The same preparation procedure as that used for preparing Pd/CeO₂-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%), O₂ (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

Fig. 1. N₂ adsorption-desorption isotherms of 0.9Pd/CeO₂ and 0.9Pd/CeO₂-nanotube. The inset shows the corresponding BJH pore diameter distributions of the samples.

Thermo Scientific Escalab 250Xi. The XPS data were calibrated using the binding energy of C 1s (284.6 eV) as standard. Microscopic structure information was obtained via transmission electron microscopy (TEM) performed on a FEI Tecnai G2 F20. CO-TPD was carried out on a Micromeritics Auto Chem II 2920. For analysis, the sample (100 mg) was reduced with 5 vol% of H₂ diluted with Ar at 300 °C for 1 h and kept under a stream of Ar for 0.5 h. After cooling the sample to room temperature, CO was supplied for 1 h and the excess CO on the sample was removed with a flow of Ar for 0.5 h. The signal was tested via online mass spectrometry. For the measurements, the samples were heated from 50 to 700 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Samples characterization

Figure 1 shows the N₂ adsorption-desorption isotherms and BJH pore size distributions of representative samples 0.9Pd/CeO₂ and 0.9Pd/CeO₂-nanotube. More specifically, 0.9Pd/CeO₂-nanotube displayed a Type IV adsorption-desorption isotherm with an H3 hysteresis loop, which is characteristic of mesoporous solids [24]. The average pore diameter of 0.9Pd/CeO₂-nanotube was ~20 nm, which is similar to the inner diameter of CeO₂ nanotubes reported in some literature

Fig. 2. XRD patterns of CeO₂ support (1), 0.9Pd/CeO₂ (2), CeO₂-nanotube support (3), and 0.9Pd/CeO₂-nanotube (4).

[23]. The surface area of the prepared samples was calculated using the BET method (Table 1). As observed, CeO₂-nanotube support featured a surface area of 58.0 m²/g, which is considerably higher than that of pure CeO₂ (2.0 m²/g). Impregnation of the CeO₂-nanotube support with a Pd NPs ethanolic solution resulted in a decrease in the specific surface area that may be due to pore blocking by the Pd species that reduces the accessibility of the nitrogen molecules to the pores.

Figure 2 shows the XRD patterns of the CeO₂ support, CeO₂-nanotube support, and corresponding Pd-containing catalysts. The samples all displayed distinct diffraction peaks at 28.6 °, 33.1 °, 47.5 °, 56.3 °, 59.1 °, 69.4 °, 76.7 °, and 79.1 °, which could be indexed to the (111), (200), (220), (311), (222), (400), (331), and (420) crystal planes of cubic fluorite-structured CeO₂ (JCPDS No. 34-394). Diffraction peaks corresponding to Pd species were not observed in the XRD patterns, indicative of the high dispersion of the Pd species with a low mass content on the supports [25,26].

TEM images of the PVP-stabilized Pd nanoparticles, CeO₂-nanotube support, 0.9Pd/CeO₂, and 0.9Pd/CeO₂-nanotube are shown in Fig. 3. As reported, Pd nanoparticles are single crystallites with a 5-shell structure [22]. Based on the statistical analysis of ~100 metal nanoparticles, the average particle size of the obtained PVP-stabilized Pd was calculated as 2.06 ± 0.56 nm (inset in Fig. 3(a)). As observed in Fig. 3(b), CeO₂-nanotube support featured a uniform tubular morpholo-

Table 1

Properties of the CeO₂ supports and CeO₂-supported Pd samples.

Sample	<i>S</i> _{BET} (m ² /g)	CO _{irr} ^a (μmol/g of catalyst)	Dispersion of Pd ^a (%)	<i>D</i> _{Pd} ^a (nm)	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺) ^b (%)	TOF ^c (s ⁻¹)
CeO ₂	2.0	—	—	—	—	—
0.9Pd/CeO ₂	1.3	13.2	2.13	>10	7.6	0.26
CeO ₂ -nanotube	58.0	—	—	—	—	—
0.3Pd/CeO ₂ -nanotube	49.9	81.9	37.9	4.5	10.4	0.34
0.6Pd/CeO ₂ -nanotube	41.0	95.7	22.6	7.5	12.0	0.53
0.9Pd/CeO ₂ -nanotube	39.3	149	23.3	7.3	12.6	0.63

^a CO_{irr} refers to the amount of irreversibly adsorbed CO and *D*_{Pd} refers to the crystallite size—both parameters were determined from CO-TPD; ^b Calculated from XPS; ^c TOF refers to the turnover frequency that represents the number of CO molecules converted per active metal site and per second at 100 °C.

Fig. 3. TEM images of PVP-stabilized Pd NPs (a), CeO₂-nanotube support (b), 0.9Pd/CeO₂-nanotube (c), and 0.9Pd/CeO₂ (d). The inset in (a) shows the particle size distribution of the PVP-stabilized Pd NPs based on the analysis of ~100 particles.

gy with tube outer diameters of ~40–60 nm. After the calcination, the Pd species were well dispersed on the CeO₂-nanotube support and their size was estimated as 3–5 nm (Fig. 3(c)). In contrast, the degree of Pd dispersion on the CeO₂ support was lower and the Pd species were larger than 5 nm (Fig. 3(d)). However, because of the high electron density of polycrystalline CeO₂ [27], and the high dispersion and small size of the Pd nanoparticles, it was difficult to resolve the interface between the Pd nanoparticles and CeO₂ nanotubes. Accordingly, the Pd nanoparticles in the TEM images in Fig. 3(c) and (d) could not be distinctly determined. Such a phenomenon has also been reported previously [28]. The dispersion and size of Pd will be discussed further in the subsequent CO-TPD analysis section.

CO-TPD is a useful tool for obtaining information on the CO adsorption ability of the samples. The CO-TPD spectra of 0.9Pd/CeO₂ and Pd/CeO₂-nanotube samples are shown in Fig. 4. The CO₂ signal was detected following CO adsorption onto the samples, thereby reflecting the amount of CO oxidized by the surface oxygen. The Pd/CeO₂-nanotube samples all displayed a strong and sharp peak at ~110 °C, a broad band at ~370 °C, and a small peak in the range of 500–700 °C, indicative of their strong CO adsorption ability. In contrast, 0.9Pd/CeO₂ did not exhibit a significant CO₂ desorption peak

Fig. 4. CO-TPD spectra of 0.9Pd/CeO₂ (1), 0.3Pd/CeO₂-nanotube (2), 0.6Pd/CeO₂-nanotube (3), and 0.9Pd/CeO₂-nanotube (4).

because of the low surface area of the sample (1.3 m²/g; Table 1) [29].

CO can also be used as a probe molecule to determine the noble metal dispersion and metal particle size on the catalyst. The adsorption of CO onto metal Pd proceeded via an irreversible linear single point attachment fashion. Because the amount of CO adsorbed irreversibly (CO_{irr}) corresponds to the number of Pd atoms, the Pd dispersion and Pd crystallite size can be estimated accordingly [30]. The calculated data are displayed in Table 1. Generally, as observed, with increasing Pd contents, CO_{irr} and *D*_{Pd} (Pd crystallite size) increased, whereas Pd dispersion decreased. Furthermore, 0.9Pd/CeO₂ exhibited a considerably lower CO_{irr} (13.2 μmol/g) than 0.9Pd/CeO₂-nanotube (149 μmol/g). The calculated Pd dispersion for 0.9Pd/CeO₂ (2.13%) was significantly lower than that for 0.9Pd/CeO₂-nanotube (23.3%). And the Pd crystallites on the CeO₂ support were larger (>10 nm) than those on the CeO₂-nanotube support (7.3 nm). Therefore, these results showed that a high dispersion of Pd particles on CeO₂ nanotube could be obtained using the present ethanol reduction method.

The XPS spectra of the Pd/CeO₂-nanotube samples and 0.9Pd/CeO₂ are given in Fig. 5. The peaks of 0.9Pd/CeO₂ were fitted with one set of spin-orbit doublets of 3d_{5/2} (336.9 eV) and 3d_{3/2} (342.3 eV), indicating that Pd was present as Pd²⁺ as bulk PdO [31]. The peaks of the Pd/CeO₂-nanotube samples at Pd 3d_{5/2} (337.6–338 eV) and Pd 3d_{3/2} (342.9–340.3 eV) indicate that Pd was mostly present as Pd²⁺. However, the Pd²⁺ XPS signals were stronger than that of bulk PdO. This result was attributed to the formation of Pd–O–Ce bonds on the catalyst surface after calcination as reported previously [32,33]. Pd²⁺ was stabilized on Ce³⁺ sites, leading to strong interactions via Pd–O–Ce bonding [34].

As observed in Fig. 5(b), the Ce 3d XPS spectra featured nine peaks labeled as V, V₀, V₁, V₂, V₃, V₄, V₅, V₆, V₇, whereby V, V₂, V₃, V₄, V₆, V₇ are characteristic of the Ce⁴⁺ 3d final states and the remaining peaks are characteristic of Ce³⁺. These results suggest the co-existence of Ce³⁺ and Ce⁴⁺ species on the surface of the catalysts [19]. Ce³⁺ sites in ceria are involved in the balance of electrostatic equilibrium and production of oxygen vacancies. The relative content of Ce³⁺ in each sample is listed in Table 1. As deduced, the relative content of Ce³⁺ decreased in the following order as 0.9Pd/CeO₂-nanotube (12.6%) > 0.6Pd/CeO₂-

Fig. 5. Pd 3d (a) and Ce 3d (b) XPS spectra of 0.9Pd/CeO₂ (1), 0.3Pd/CeO₂-nanotube (2), 0.6Pd/CeO₂-nanotube (3), and 0.9Pd/CeO₂-nanotube (4).

nanotube (12.0%) > 0.3Pd/CeO₂-nanotube (10.4%) > 0.9Pd/CeO₂ (7.6%). It was evident that the relative content of Ce³⁺ on the Pd/CeO₂-nanotube catalysts increased with increasing contents of Pd. Accordingly, 0.9Pd/CeO₂-nanotube is expected to provide a higher number of oxygen vacancies when compared with 0.9Pd/CeO₂ owing to the higher content of Ce³⁺ on the Pd/CeO₂-nanotube surface.

3.2. Catalytic activity

Figure 6 shows the light-off curves of CO oxidation over 0.9Pd/CeO₂ and Pd/CeO₂-nanotube catalysts. As observed, with increasing reaction temperatures, the catalytic activities toward CO oxidation improved for all catalysts studied. CeO₂-nanotube, 0.3Pd/CeO₂-nanotube, 0.6Pd/CeO₂-nanotube, 0.9Pd/CeO₂-nanotube, and 0.9Pd/CeO₂ respectively yielded *T*₅₀ values (temperature corresponding to 50% CO conversion) of 275, 118, 96, 62, and 152 °C, and *T*₁₀₀ values (temperature corresponding to 100% CO conversion) of 320, 180, 140, 100, and 200 °C. The results showed that the Pd/CeO₂-nanotube catalysts exhibited considerably higher activities than 0.9Pd/CeO₂. Among the prepared catalysts, 0.9Pd/CeO₂-nanotube showed the highest activity.

To gain insights into the intrinsic activities of the CeO₂-supported Pd catalysts, the turnover frequency (TOF) was calculated based on the conversion level of CO and metal dispersion [35]. The results are listed in Table 1. The TOF values over 0.9Pd/CeO₂, 0.3Pd/CeO₂-nanotube, 0.6Pd/CeO₂-nanotube, 0.9Pd/CeO₂-nanotube at 100 °C were 0.26, 0.34, 0.53, and 0.63 s⁻¹, respectively. The Pd/CeO₂-nanotube catalysts displayed higher TOFs than 0.9Pd/CeO₂. Among all samples, 0.9Pd/CeO₂-nanotube exhibited the highest TOF. The TOF results were consistent with those of the light-off curves shown in Fig. 6.

Arrhenius plots for the different catalysts were derived us-

ing a method reported in the literature [36], and are shown in Fig. 7. The activation energy (*E*_a) values for 0.9Pd/CeO₂, 0.3Pd/CeO₂-nanotube, 0.6Pd/CeO₂-nanotube, and 0.9Pd/CeO₂-nanotube were 58.6, 36.9, 32.3, and 26.5 kJ/mol, respectively. With increasing Pd contents from 0.3 to 0.9 wt% on the CeO₂-nanotube support, *E*_a decreased slightly, suggesting that CO oxidation over these catalysts proceeded via similar reaction pathways [36]. In contrast, 0.9Pd/CeO₂ displayed a considerably higher *E*_a than the Pd/CeO₂-nanotube catalysts, thereby suggesting that CO oxidation over this catalyst proceeded via a different reaction pathway. Regardless, it could be deduced that the oxidation of CO over 0.9Pd/CeO₂-nanotube was the most favorable.

It is generally believed that the interface between the metal and oxide support provides the active sites for a given catalytic

Fig. 6. Light-off curves of CO oxidation over CeO₂-nanotube support (1), 0.9Pd/CeO₂ (2), 0.3Pd/CeO₂-nanotube (3), 0.6Pd/CeO₂-nanotube (4), and 0.9Pd/CeO₂-nanotube (5).

Fig. 7. Arrhenius plots for CO oxidation over 0.9Pd/CeO₂ (1), 0.3Pd/CeO₂-nanotube (2), 0.6Pd/CeO₂-nanotube (3), and 0.9Pd/CeO₂-nanotube (4).

reaction. Also, CO oxidation over supported Pd catalysts follows a Langmuir-Hinshelwood mechanism. More specifically, the reaction proceeds as follows [15,19]: (1) CO adsorbs onto the surface of Pd species; (2) the adsorbed CO reacts with surface active species oxygen, including active lattice oxygen on PdO or CeO₂ and adsorbed oxygen, to produce CO₂; and (3) the catalyst generates new oxygen vacancies, which are promptly filled with O₂ from the reaction gas to subsequently complete the redox recycle.

Based on the above-discussed results and proposed mechanism, it is clear that the metal size, structure of the support, CO adsorption ability, and metal-ceria interaction are the key factors that influence the catalytic performance. According to the characterization results, relative to the Pd/CeO₂ catalyst, the Pd/CeO₂-nanotube catalysts exhibit larger BET surface areas

(Table 1), which favor Pd dispersion. It is in agreement of dispersion and size results obtained by CO-TPD (Table 1) that Pd/CeO₂-nanotube has higher metal dispersion and smaller particle size than those of Pd/CeO₂. The higher CO adsorption ability (Fig. 4) is beneficial to Step (1) in the Langmuir-Hinshelwood mechanism. From the XPS results, the Pd/CeO₂-nanotube catalysts can provide more oxygen vacancies owing to the higher content of Ce³⁺ (Table 1) on the surface. The better interaction, enhanced by Pd–O–Ce bonding (Fig. 4), between the metal and support is favorable to Step (2). Furthermore, the mesoporous structure (Fig. 1) of the Pd/CeO₂-nanotube catalysts favors the adsorption and diffusion of reactant and product gases [37]. The lower activation energies of the Pd/CeO₂-nanotube catalysts (Fig. 7) prove that the catalytic reaction over the catalysts proceeds via a different pathway (which is favorable toward CO oxidation) from that occurring over the Pd/CeO₂ catalyst. Accordingly, the Pd/CeO₂-nanotube catalysts displayed better redox abilities and better catalytic activities toward CO oxidation (Fig. 6) than the Pd/CeO₂ catalyst.

4. Conclusions

In this work, we have prepared CeO₂-supported Pd nanoparticles and investigated their catalytic performance toward CO oxidation. Compared with pure CeO₂, the mesoporous and tubular structure of the CeO₂-nanotube support improved the dispersion of Pd species and accordingly enhanced CO adsorption. The abundant amounts of Ce³⁺ on the nanotube surface promoted the formation of oxygen vacancies that are important for oxygen activation. The Pd–O–Ce interactions on the nanotube are responsible for the reaction.

References

- [1] Y. Zeng, L. Qiao, Y. F. Bing, M. Wen, B. Zou, W. T. Zheng, T. Zhang, G.

Graphical Abstract

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The preparation of CeO₂ nanotube-supported Pd nanoparticles and their catalytic performance toward CO oxidation were described. Abundant Ce³⁺ and Pd–O–Ce interactions on the nanotube facilitated the reaction.

- T. Zou, *Sens. Actuators B*, **2012**, 173, 897.
- [2] T. Y. Wang, L. D. Li, N. J. Guan, *Fuel Process. Technol.*, **2013**, 108, 41.
- [3] X. D. Zhang, Z. P. Qu, F. L. Yu, Y. Wang, *Chin. J. Catal.*, **2013**, 34, 1277.
- [4] Y. Zhou, Z. Y. Wang, C. J. Liu, *Catal. Sci. Technol.*, **2015**, 5, 69.
- [5] G. J. Hutchings, M. Hartuta, *Appl. Catal. A*, **2005**, 291, 2.
- [6] J. M. Campelo, D. Luna, R. Luque, J. M. Marinas, A. A. Romero, *ChemSusChem*, **2009**, 2, 18.
- [7] P. Bera, A. Gayen, M. S. Hegde, N. P. Lalla, L. Spadaro, F. Frusteri, F. Arena, *J. Phys. Chem. B*, **2003**, 107, 6122.
- [8] S. N. Pavlova, V. A. Sadykov, N. N. Bulgakov, M. N. Bredikhin, *J. Catal.*, **1996**, 161, 517.
- [9] A. M. Venezia, L. F. Liotta, G. Deganello, Z. Schay, D. Horvath, L. Guzzi, *Appl. Catal. A*, **2001**, 211, 167.
- [10] S. Y. Wang, N. Li, R. M. Zhou, L. Y. Jin, G. S. Hu, J. Q. Lu, M. F. Luo, *J. Mol. Catal. A*, **2013**, 374, 53.
- [11] M. Q. Shen, G. X. Wei, H. M. Yang, J. Wang, X. Q. Wang, *Fuel*, **2013**, 103, 869.
- [12] G. Glaspell, H. M. A. Hassan, A. Elzatahry, V. Abdalsayed, M. S. El-Shall, *Top. Catal.*, **2008**, 47, 22.
- [13] G. Q. Yi, Z. N. Xu, G. C. Guo, K. I. Tanaka, Y. Z. Yuan, *Chem. Phys. Lett.*, **2009**, 479, 128.
- [14] J. Y. Luo, M. Meng, H. Xian, Y. B. Tu, X. G. Li, T. Ding, *Catal. Lett.*, **2009**, 133, 328.
- [15] H. Q. Zhu, Z. F. Qin, W. J. Shan, W. J. Shen, J. G. Wang, *J. Catal.*, **2005**, 233, 41.
- [16] M. S. Hegde, G. Madras, K. C. Patil, *Acc. Chem. Res.*, **2009**, 42, 704.
- [17] Y. Zhu, S. R. Zhang, J. J. Shan, L. Nguyen, S. H. Zhan, X. L. Gu, F. Tao, *ACS Catal.*, **2013**, 3, 2627.
- [18] D. Mendez, R. Vargas, C. Borrás, S. Blanco, J. Mostany, B. R. Scharifker, *Appl. Catal. B*, **2015**, 166, 529.
- [19] Y. F. Su, Z. C. Tang, W. L. Han, P. Zhang, Y. Song, G. X. Lu, *CrystEngComm*, **2014**, 16, 5189.
- [20] K. B. Zhou, Z. Q. Yang, S. Yang, *Chem. Mater.*, **2007**, 19, 1215.
- [21] T. Teranishi, M. Miyake, *Chem. Mater.*, **1998**, 10, 594.
- [22] Y. H. Zhang, N. Zhang, Z. R. Tang, Y. J. Xu, *ACS Sust. Chem. Eng.*, **2013**, 1, 1258.
- [23] X. B. Zhao, J. You, X. W. Lu, Z. G. Chen, *J. Inorg. Mater.*, **2011**, 26, 159.
- [24] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, T. Siemieniewska, *Pure Appl. Chem.*, **1985**, 4, 603.
- [25] M. F. Luo, Z. Y. Hou, X. X. Yuan, X. M. Zheng, *Catal. Lett.*, **1998**, 50, 205.
- [26] H. Guo, Y. B. He, Y. P. Wang, L. X. Liu, X. J. Yang, S. X. Wang, Z. J. Huang, Q. Y. Wei, *J. Mater. Chem. A*, **2013**, 1, 7494.
- [27] M. Cargnello, N. L. Wieder, T. Montini, R. J. Gorte, P. Fornasiero, *J. Am. Chem. Soc.*, **2010**, 132, 1402.
- [28] Z. R. Tang, X. Yin, Y. H. Zhang, N. Zhang, Y. J. Xu, *Chin. J. Catal.*, **2013**, 34, 1123.
- [29] M. S. Jin, J. N. Park, J. K. Shon, Z. H. Li, M. Y. Yoon, H. J. Na, Y. K. Park, J. M. Kim, *Res. Chem. Intermed.*, **2011**, 37, 1181.
- [30] K. V. R. Chary, D. Naresh, V. Vishwanathan, M. Sadakane, W. Ueda, *Catal. Commun.*, **2007**, 8, 471.
- [31] T. Pillo, R. Zimmermann, P. Steiner, S. Hufner, *J. Phys. Condens. Matter.*, **1997**, 9, 3987.
- [32] S. Hinokuma, H. Fujii, M. Okamoto, K. Ikeue, M. Machida, *Chem. Mater.*, **2010**, 22, 6183.
- [33] E. M. Slavinskaya, R. V. Gulyaev, A. V. Zadesenets, O. A. Stonkus, V. I. Zaikovskii, Y. V. Shubin, S. V. Korenev, A. I. Boronina, *Appl. Catal. B*, **2015**, 166–167, 91.
- [34] K. R. Priolkar, P. Bera, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, N. P. Lalla, *Chem. Mater.*, **2002**, 14, 2120.
- [35] H. H. Liu, Y. Wang, A. P. Jia, S. Y. Wang, M. F. Luo, J. Q. Lu, *Appl. Surf. Sci.*, **2014**, 314, 725.
- [36] L. Q. Liu, F. Zhou, L. G. Wang, X. J. Qi, F. Shi, Y. Q. Deng, *J. Catal.*, **2010**, 274, 1.
- [37] M. S. Jin, J. N. Park, J. K. Shon, J. H. Kim, Z. H. Li, Y. K. Park, J. M. Kim, *Catal. Today*, **2012**, 185, 183.

CeO₂纳米管负载Pd纳米颗粒催化CO低温氧化

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摘要: 高效负载型Pd催化剂的制备及其在CO低温氧化反应中的机理探究是近年来的研究热点。普遍认为, Pd催化剂上的CO氧化反应遵循Langmuir-Hinshelwood机理: 首先, CO吸附于Pd物种表面; 然后, CO与催化剂表面的晶格氧发生反应转化为CO₂, 反应发生在金属-载体界面。另外, 高分散的Pd活性物种有利于CO氧化反应。同时载体的形貌、暴露的晶面、氧空位以及孔结构等都是影响催化剂活性的重要因素。CeO₂纳米管具有独特的管状特征和较高的比表面积, 是一种潜在的CO低温氧化催化剂载体。

本文利用乙醇还原法, 以CeO₂纳米管为载体, 制备不同Pd含量的Pd/CeO₂-nanotube纳米催化剂, 并利用N₂吸附脱附、X射线衍射(XRD)、透射电子显微镜(TEM)、CO程序升温脱附(CO-TPD)、X射线光电子能谱(XPS)等表征手段, 探索纳米催化剂载体形貌对CO氧化反应活性的影响。氮气吸脱附结果表明, Pd/CeO₂-nanotube具有较高的比表面积(58.0 m²/g), 且存在介孔结构。XRD表征发现, Pd/CeO₂-nanotube的衍射峰对应立方萤石型结构的CeO₂的(111), (200), (220), (311)等晶面。TEM结果表明, Pd/CeO₂-nanotube具有均匀的纳米管形貌, 其外径为40–60 nm, Pd纳米颗粒均匀分散在其表面。CO-TPD结果表明, Pd/CeO₂-nanotube在110 °C附近具有很强的脱附峰, 在370 °C和600 °C附近分别具有较宽和较弱的脱附峰, 这表明该催化剂具有较多的吸附位, 且具有很强的CO吸附能力; CO不可逆吸附量计算结果表明, 该催化剂上的Pd具有很高的表面分散度(23.3%), Pd颗粒尺寸为7.3 nm。XPS表征显示, Pd以Pd²⁺的形式分散于CeO₂纳米管的表面, 且与载体发生相互作用, 存在Pd–O–Ce键; 同时该催化剂表面存在丰富的Ce³⁺, 为反应提供更多的氧空位。0.9Pd/CeO₂-nanotube纳米催化剂在CO氧化反应中表现出优良的活性, 能在100 °C实现CO的完全转化; 通过计算发现, 该催化剂具有较高的TOF值(0.63 s⁻¹), 由Arrhenius

曲线可得到该催化剂的活化能为26.5 kJ/mol.

综上所述: 金属活性组分的尺寸和分散度、载体的结构特征、CO吸附能力以及金属-载体间的相互作用决定催化剂的性能. Pd/CeO₂-nanotube的高比表面积有利于Pd的分散; 其强CO吸附能力有利于CO吸附于Pd物种表面; 催化剂表面丰富的Ce³⁺能为反应提供更多的氧空位, Pd-O-Ce键的形成能增强金属-载体间的相互作用, 有利于CO与催化剂表面晶格氧发生反应. 同时催化剂介孔结构有利于反应气体和产物气体的吸附和扩散, 因此, Pd/CeO₂-nanotube纳米催化剂在CO氧化反应中表现出优良的活性.

关键词: 氧化铈纳米管; 钯纳米颗粒; 金属-载体相互作用; 一氧化碳氧化; 低温

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