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Article

Inhibiting Pd nanoparticle aggregation and improving catalytic performance using one-dimensional CeO₂ nanotubes as support

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ARTICLE INFO

Article history:

Received 23 November 2012

Accepted 25 December 2012

Published 20 June 2013

Keywords:

Ceria

Nanotube

Palladium

Nanoparticle

Support effect

Selective oxidation

ABSTRACT

One-dimensional (1D) CeO₂ nanotubes can be used as a support to inhibit Pd nanoparticle aggregation during the high temperature calcination process in air. This is in opposition to the significant aggregation of Pd particles that is observed for the preparation of supported Pd metal catalysts using non-1D commercial CeO₂ as support. The as-prepared Pd/CeO₂ nanotube catalyst exhibits much higher catalytic performance than Pd/commercial CeO₂ toward the aerobic selective oxidation of benzyl alcohol to benzaldehyde. This work suggests that 1D metal oxide materials can be used as a promising class of supports to inhibit noble metal nanoparticle aggregation, thereby improving catalytic performance toward target reactions.

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1. Introduction

Supported noble metal nanoparticles (NPs) have been used widely for various important catalytic redox reactions in heterogeneous catalysis [1–11]. In particular, the selective oxidation over the catalyst of supported noble metal NPs is a well-established approach for the synthesis of fine chemicals [5]. In addition to the effect of size and shape of noble metal NPs on catalytic activity, the nature of the supporting matrix has been well recognized as a key factor capable of influencing the size, shape, or dimension of noble metal NPs during the catalyst preparation process and in turn affects the catalytic activity of supported noble metal NPs [1–6,12–17]. Typical examples in this regard have been observed in the use of nanocrystalline CeO₂ supports to prepare small noble metal NPs

with high activity toward gas-phase CO oxidation under ambient conditions [18,19]. For example, Corma's group reported that nanocrystalline CeO₂ with small particle size, ca. 5 nm, can be used as an active support to prepare Au/CeO₂ (which is more active than Au on a CeO₂ support with large particle size) and commercially active Au/TiO₂ catalysts under ambient conditions [19]. Tang et al. [18] demonstrated that nanocrystalline CeO₂ prepared by precipitation of a solution of the acetate using supercritical CO₂ as an antisolvent can not only be used as a support for high-activity Au catalysts toward CO oxidation under ambient conditions, but can also promote the high dispersion of Au nanoparticles.

We for the first time demonstrate that one-dimensional (1D) CeO₂ nanotubes can be used as specific supports to prevent the aggregation of Pd NPs during the calcination process.

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This work was supported by the National Natural Science Foundation of China (20903022, 20903023), the Science and Technology Development of Foundation of Fuzhou University (2009-XQ-10), the Open Fund of Photocatalysis of Fuzhou University (0380038004), and Program for Returned High-level Overseas Chinese Scholars of Fujian Province.

DOI: 10.1016/S1872-2067(12)60536-1 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 34, No. 6, June 2013

In contrast, obvious aggregation of Pd NPs is observed when using commercial CeO_2 to prepare supported Pd catalysts. In particular, compared with Pd/commercial CeO_2 , Pd/ CeO_2 nanotubes show remarkably enhanced catalytic activity for the selective oxidation of benzyl alcohol to benzaldehyde in a liquid phase. This suggests the promising potential of using 1D metal oxide materials as supports to prepare a noble metal NP catalyst with anti-aggregation and improved catalytic performance.

2. Experimental

2.1. Catalyst preparation

Commercial CeO_2 was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). CeO_2 nanotubes were prepared by the hydrothermal treatment of $\text{Ce}(\text{OH})\text{CO}_3$ precursors with NaOH solution as reported previously [20]. To prepare supported 5 wt% Pd catalysts, the support of commercial CeO_2 or CeO_2 nanotube was impregnated with a desired amount of colloidal Pd solution synthesized by an alcohol reduction method in the presence of polyvinylpyrrolidone [21–23]. The final catalysts, Pd/commercial CeO_2 and Pd/ CeO_2 nanotubes, were obtained by calcination at 673 K for 2 h in air.

2.2. Catalyst characterization

The phase composition of the samples was determined by X-ray diffraction (XRD) on a Philip X' Pert Pro MPP X-ray diffractometer. The microscopic structure information was determined by transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCA Lab250 spectrometer with a monochromatic Al $K\alpha$ as X-ray source. All binding energies were calibrated using the C 1s peak of the surface adventitious carbon at 284.6 eV.

2.3. Catalytic activity test

A mixture of 50 mg catalyst and 20 ml benzyl alcohol was transferred into a Parr autoclave reactor (MINI-REACTOR, SNAP-TITE, INC. USA) and stirred for 30 min to ensure an even blend of catalyst in solution. The autoclave was purged 5 times with oxygen to obtain a desired pressure of 3×10^5 Pa. The stirrer speed was set at 1500 r/min and the reaction mixture was heated to 373 K. Samples were analyzed by Agilent Gas Chromatograph (GC-7820). Conversion of benzyl alcohol and the selectivity for benzaldehyde were defined as:

$$\text{Conversion (\%)} = [(C_0 - C_{\text{BA}})/C_0] \times 100\%$$

$$\text{Selectivity (\%)} = [C_{\text{BAD}}/(C_0 - C_{\text{BA}})] \times 100\%$$

where C_0 is the initial concentration of benzyl alcohol and C_{BA} and C_{BAD} are the concentration of benzyl alcohol and benzaldehyde, respectively, at a certain time after the catalytic reaction.

3. Results and discussion

Figure 1 shows the XRD spectra of Pd/ CeO_2 nanotubes,

Fig. 1. XRD patterns of Pd/commercial CeO_2 (1), commercial CeO_2 (2), Pd/ CeO_2 nanotubes (3), and CeO_2 nanotubes (4).

Fig. 2. SEM (a), TEM (b) images and outer diameter distribution (e) of CeO_2 nanotubes, TEM (c) and HRTEM (d) images of Pd/ CeO_2 nanotubes, TEM image of Pd NPs (f) (upper and lower insets are the corresponding selected area electron diffraction pattern and HRTEM image, respectively), and EDX analysis of selected local areas of Pd/ CeO_2 nanotubes (g, h).

Pd/commercial CeO₂, CeO₂ nanotubes, and commercial CeO₂. All distinctive peaks are ascribed to diffraction from crystalline CeO₂ (JCPDS 34-394) [20]. The peaks located at $2\theta = 28.6^\circ$, 33.1° , 47.5° , 56.3° , 59.1° , 69.4° , 76.7° , and 79.1° can be indexed to (111), (200), (220), (311), (222), (400), (331), and (420) crystal planes of cubic fluorite-structured CeO₂. No noble metal Pd NP diffraction peaks were observed in the XRD spectra, possibly because of the high dispersion of Pd NPs with low weight content on the CeO₂ support. Such a phenomenon has also been found in previous reports [24,25].

Figure 2 shows the morphological analysis of the as-prepared CeO₂ nanotubes, Pd NPs, and Pd/CeO₂ nanotube catalyst. The SEM and TEM images in Fig. 2(a) and (b) show that the CeO₂ nanotubes have a uniform morphology with outer diameter of approximately 30–60 nm and a wall thickness of ca. 5–10 nm. The as-synthesized Pd NPs have diameters of 2–4 nm with polycrystalline structure as reflected in Fig. 2(f) and its insets, which is consistent with previous reports [21–23]. In the TEM and high resolution TEM (HRTEM) images of the Pd/CeO₂ nanotubes (Fig. 2(c) and (d)), no typical Pd NPs were distinguished from the TEM analysis. Because of the high electron density of polycrystalline CeO₂ [26] and the small size of the Pd NPs, it is very difficult to resolve the interface between the Pd NPs and the CeO₂ nanotubes. However, elemental dispersive X-ray (EDX) analysis on selected local areas shows Pd NP signals (Fig. 2(g) and (h)). Considering the small size of the original Pd colloidal particles, it can be concluded that the Pd NPs do not undergo significant aggregation during the preparation of Pd supported on CeO₂ nanotubes.

XPS analysis in Fig. 3 on the Pd/CeO₂ nanotubes further shows two typical peaks located around 335.4 and 340.8 eV, indicating the metallic state of the Pd nanoparticles [21,27]. However, the case is remarkably different for the Pd catalyst supported on commercial CeO₂. As shown in Fig. 4, obvious aggregation of Pd NPs with sizes in the range of 10–40 nm is observed. Therefore, it is clear that the CeO₂ nanotubes can be used as a support for effective prevention of the aggregation of Pd NPs.

The surface area and porosity of the Pd/CeO₂ nanotubes and Pd/commercial CeO₂ were investigated. As displayed in Fig. 5,

Fig. 3. Pd 3d XPS profile for Pd/CeO₂ nanotube catalyst.

both samples exhibit a type IV adsorption-desorption isotherm with typical H3 hysteresis loop, characteristic of mesoporous solids according to the IUPAC classification [28]. The BET surface area of the Pd/CeO₂ nanotubes is ca. 81 m²/g, which is much larger than that of Pd/commercial CeO₂ (24 m²/g). This should be because of the specific structure of the 1D CeO₂

Fig. 5. N₂ adsorption-desorption isotherms of Pd/CeO₂ nanotubes and Pd/commercial CeO₂. The inset is the corresponding pore diameter distribution.

Fig. 4. TEM image of Pd/commercial CeO₂ and EDX analysis of selected local areas.

Fig. 6. Time-online catalytic activity of Pd/CeO₂ nanotubes and Pd/commercial CeO₂ toward the selective oxidation of benzyl alcohol to benzaldehyde.

nanotubes and its function in inhibiting the aggregation of Pd NPs, and should be beneficial for improving the catalytic performance of a sample for a given reaction.

The catalytic performance of the Pd/CeO₂ nanotubes and the Pd/commercial CeO₂ was evaluated by the aerobic oxidation of benzyl alcohol to benzaldehyde. Figure 6 shows the time online data of activity and selectivity for oxidation of benzyl alcohol over the two catalysts. Blank experiments using the bare support of commercial CeO₂ and CeO₂ nanotubes show only trace conversion of benzyl alcohol, suggesting that the Pd NPs serve as the main active components for the oxidation of benzyl alcohol. The trace conversion of the substrate is also observed under anaerobic conditions, indicating that dissolved oxygen functions as the oxidant. The Pd/CeO₂ nanotubes exhibit a much higher catalytic activity than Pd/commercial CeO₂. After 8 h, the conversion of benzyl alcohol over the Pd/CeO₂ nanotubes reaches ca. 40%, which is four times higher than that over Pd/commercial CeO₂. It has been estimated that the turnover frequency of the Pd/CeO₂ nanotubes is ca. 20 times higher than that of Pd/commercial CeO₂ for the selective oxidation of benzyl alcohol to benzaldehyde. In addition, it should be noted that longer reaction times will lower the selectivity for benzaldehyde moderately, because oxidation leads to the pro-

Fig. 7. Recycled testing catalytic activity of Pd/CeO₂ nanotubes toward the selective oxidation of benzyl alcohol to benzaldehyde at 373 K (oxygen pressure of 3×10^5 Pa).

duction of some benzoic acid as a by-product.

Activity testing on recycled Pd/CeO₂ nanotubes has also been carried out. The result shows that this catalyst is stable and reusable under these experimental conditions. As reflected in Fig. 7, after three recycling activity tests for the selective oxidation of benzyl alcohol to benzaldehyde, there is no significant decline in the conversion of benzyl alcohol over the used Pd/CeO₂ nanotubes. Therefore, the as-prepared Pd/CeO₂ nanotubes can serve as an efficient and stable catalyst for the selective aerobic oxidation of benzyl alcohol to benzaldehyde.

4. Conclusions

The 1D CeO₂ nanotubes can be utilized as a support to prevent the aggregation of Pd nanoparticles. This is remarkably different from the case of commercial CeO₂ supports. The Pd/CeO₂ nanotube catalyst exhibits a much higher catalytic performance than Pd/commercial CeO₂ toward the aerobic oxidation of benzyl alcohol to benzaldehyde. This suggests that 1D metal oxide materials are a class of promising supports to prepare noble metal nanoparticles with anti-aggregation and enhanced catalytic performance for specific oxidation processes.

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Graphical Abstract

Chin. J. Catal., 2013, 34: 1123–1127 doi: 10.1016/S1872-2067(12)60536-1

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One-dimensional CeO₂ nanotubes serve as a support to inhibit Pd nanoparticle aggregation and improve catalytic performance toward selective oxidation as opposed to using commercial CeO₂ as a support.

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一维CeO₂纳米管载体对Pd纳米粒子团聚的抑制及催化性能的提高

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摘要: 用一维CeO₂纳米管替代非一维结构的商用CeO₂, 用于负载Pd而制得的催化剂在空气气氛下高温煅烧过程中Pd纳米粒子的团聚受到明显抑制, 在选择性有氧化苯甲醇生成苯甲醛反应中, 所制CeO₂纳米管负载的Pd催化剂表现出更高的催化活性. 可见, 一维金属氧化物材料有望用作载体以抑制贵金属纳米粒子的团聚, 从而提高其催化性能.

关键词: 二氧化铈; 纳米管; 钯; 纳米粒子; 载体效应; 选择性氧化

收稿日期: 2012-11-23. 接受日期: 2012-12-25. 出版日期: 2013-06-20.

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基金来源: 国家自然科学基金(20903022, 20903023); 福州大学科学技术发展基金(2009-XQ-10); 福州大学光催化开放基金(0380038004); 福建省海外高层次人才回国人员项目.

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