available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

The enhanced Fenton-like catalytic performance of PdO/CeO₂ for the degradation of acid orange 7 and salicylic acid

Lin Ge, Chengjie Zang, Feng Chen *

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China

ARTICLE INFO

Article history:

Received 21 October 2014

Accepted 1 December 2014

Published 20 March 2015

Keywords:

Fenton-like reaction

Ceria

Palladium oxide

Degradation

Hydrogen peroxide

ABSTRACT

A PdO/CeO₂ catalyst was prepared by deposition-precipitation method and characterized with X-ray diffraction, high-resolution transmission electron microscopy, N₂ adsorption-desorption, X-ray photoelectron spectroscopy and Raman spectroscopy. The results show that the Pd is presented as Pd²⁺ in the catalyst. The interaction between the deposited PdO and CeO₂ increases the Ce³⁺ content. The catalytic activity of PdO/CeO₂ was tested in the heterogeneous Fenton-like degradation of acid orange 7 (AO7) and salicylic acid (SA), both in the dark and under visible irradiation. Deposition of PdO accelerates the Fenton-like degradation of SA, which reaches a maximum at 1.0 atom% PdO loading. A dye sensitization effect was seen with AO7 under visible irradiation. Dye sensitization promotes the regeneration of Ce³⁺ by interfacial peroxides species through interfacial electron injection. Consequently, the combined effects of PdO loading and visible light irradiating enhanced the Fenton-like activity to a reaction rate constant of 3.90 h⁻¹ for the 1.0 PdO/CeO₂, a ca. 50-fold improvement.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

As an important catalytic material, CeO₂ has attracted growing interest in various catalytic applications (for example, three-way catalysis, water-gas shift reaction, and catalytic wet air oxidation), due to its rich oxygen vacancies and low redox potential between Ce³⁺ and Ce⁴⁺ [1–4]. To improve the catalytic performance, many techniques have been applied to Ce-containing materials, including ion doping, noble metal loading, and multi-metal oxide compositing [4–6]. In particular, noble metal loaded oxides have aroused much interest for application as heterogeneous catalysts [1,6,7].

Recently, the strong metal-support interaction (SMSI) has been verified at the interface between noble metal and an oxides support, which dramatically changes the property of cata-

lysts and favors their catalytic activity. For instance, introducing Au on the surface of ZnO greatly improves the catalytic activity for the CO oxidation by a SMSI interaction, via electron transfer from Au to the ZnO support [8]. Similarly, a Ce³⁺ content increase and catalytic activity enhancement were observed via the SMSI interaction by loading the catalyst with Pt [9], Pd [7], or Au [10] clusters on the surface of CeO₂. In general, smaller particle size, larger interfaces, and good thermal stability favor the catalytic activity in a noble metal loaded CeO₂ (e.g., Pt/CeO₂) catalyst for CO oxidation [11].

Pd species, in the form of metallic Pd and cationic Pd, are of particular interest in CeO₂ catalysis owing to their excellent catalytic performance. Due to SMSI interactions [12], cationic Pd species are generated by electron transfer from the Pd particles to the CeO₂ support, and this results in a significantly en-

* Corresponding author. Tel: +86-21-64253056; E-mail: fengchen@ecust.edu.cn

This work was supported by the National Natural Science Foundation of China (21177039) and the Innovation Program of Shanghai Municipal Education Commission (13ZZ042).

DOI: 10.1016/S1872-2067(14)60261-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 3, March 2015

hanced activity for Pd/CeO₂ in the synthesis of methanol from CO [13]. PdO has been reported to provide sites for CO chemisorption on surface, while PdO species in the CeO₂ matrix generate oxygen vacancies that activate O₂ in the catalytic oxidation of CO [14]. The chemisorption and catalytic performance of these Pd-O sites were also discussed by Colussi et al. [15].

Ce salts have been reported to have Fenton-like reactivity in the degradation of organic materials in aqueous solutions [16]. As an ambient catalytic reaction, a heterogeneous Fenton-like system, based on the CeO₂ and H₂O₂, has been developed in our previous studies [17–23]. Similar to those occurring at high temperatures (> 600 °C) with CeO₂ catalysis, as the Ce³⁺ content increases, the catalytic performance also improves for heterogeneous Fenton-like degradation reactions [18,23]. For instance, Au nanocluster loading increases the Ce³⁺ content in CeO₂ catalysts, thus promoting the Fenton-like catalytic activity of CeO₂ in the degradation of acid orange 7 (AO7) [23].

PdO loading has improved the catalytic performance of high temperature (> 600 °C) CeO₂ catalysts [14–15]. We choose to investigate PdO/CeO₂ for use in ambient temperature heterogeneous Fenton-like reactions. Therefore, PdO/CeO₂ catalysts were prepared by deposition-precipitation method. The heterogeneous Fenton-like degradations of AO7 and salicylic acid (SA) were tested to reveal the role of PdO in the catalytic activity of CeO₂ both in the dark and under visible irradiation.

2. Experimental

2.1. Reagents and materials

Ce(NO₃)₃·6H₂O and PdCl₂ were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd in Shanghai, China. NH₃·H₂O (28%) and H₂O₂ (30%) were supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd in Shanghai, China. AO7 dye and SA were obtained from Acros and Shanghai Lingfeng Chemical Reagent Co., Ltd, respectively. All reagents were of analytical grade and used as received without further purification. Ultra-pure water (18 MΩ/cm) was used throughout the experiments.

2.2. Preparation of CeO₂ and PdO/CeO₂

The precipitation method reported in our previous work [19] was employed to synthesize CeO₂. NH₃·H₂O (6 mL, 28%) was added dropwise to a Ce(NO₃)₃ solution (0.1 mol/L, 150 mL) with vigorous stirring to form a yellowish suspension. The suspension was stirred continuously for 2 h at 40 °C followed by aging for 12 h at 40 °C. The resulting purple precipitate was collected by centrifugation, washed several times with water, and dried at 60 °C under vacuum for 12 h. After grinding, the precipitate was heated to 500 °C at 2 °C/min before being calcined at this temperature in air for 4 h to obtain the raw CeO₂ powder.

The PdO/CeO₂ catalyst was prepared by deposition-precipitation (DP) [24]. Raw CeO₂ powder (0.86 g) was dispersed in 100 mL H₂O, and the desired amount of PdCl₂ was added to the suspension with vigorous stirring. Palladium hydroxide was

precipitated on the CeO₂ by the addition of 2.0 mol/L NaOH, maintaining the pH of the solution at 8.5. During the precipitation process, the suspension was stirred for 2 h at 70 °C. The precipitation was washed several times with water and dried at 60 °C under vacuum for 12 h to obtain the PdO/CeO₂. According to the amount of PdCl₂, described by the molar percent of Pd used, the as-prepared catalysts were labeled as CeO₂, 0.05 PdO/CeO₂, 0.1 PdO/CeO₂, 0.5 PdO/CeO₂, 1.0 PdO/CeO₂ and 2.0 PdO/CeO₂, respectively.

2.3. Catalyst characterization

X-ray diffraction (XRD) analysis of the catalysts was carried out with a Rigaku Ultima IV apparatus using Cu K_α radiation (λ = 0.15406 nm) and a graphite monochromator at room temperature, operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ range of 5°–80°. The BET specific surface areas of the samples were determined by N₂ adsorption-desorption at –196 °C (Micromeritics ASAP 2020M). Samples were degassed at 180 °C for 10 h prior to the measurement. Raman measurements were performed at room temperature using a Renishaw Via+ Reflex Raman spectrometer with the excitation wavelength of 514.5 nm. The X-ray photoelectron spectroscopy (XPS) instrument was a Thermo Fisher ESCALAB 250Xi system with Al K_α radiation (photon energy 1361 eV), and calibrated internally by the carbon deposit C (1s) binding energy (BE) at 284.6 eV. The shift of the binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. The morphology of the samples was observed by high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2000-EX) with an electron beam operating at an accelerating voltage of 200 kV.

2.4. Catalytic activity test

The catalytic activity of the catalysts was evaluated in the dark and under visible irradiation. To avoid any interference from organics desorption, all reactions were carried out in a pre-mixed mode [19], i.e., the CeO₂ was first mixed with H₂O₂ before the addition of the organic substances. In the Fenton-like reaction, 0.025 g catalyst powder was mixed with 1.4 mL H₂O₂ (5%, prepared in advance) and the mixture was stirred for 5 min. Then, 50 mL of the aqueous organic solution (AO7 of 35 mg/L or SA of 20 mg/L, pH 4.0) was added into the mixture at the start of the reaction time. At the given time intervals, samples (3 mL) were taken from the mixture and immediately centrifuged. The supernatant solution was withdrawn and analyzed by recording the absorbance at 484 nm (for AO7) or 296 nm (for SA) with a UV-Vis spectrophotometer (Shimadzu UV-2450).

As for a typical visible light irradiated experiment (photo-Fenton reaction), a 500-W tungsten halogen lamp equipped with a UV cut-off filter (λ > 420 nm) was used as a visible light source. The lamp was cooled with flowing water in a quartz cylindrical jacket around the lamp, and ambient temperature was maintained during the whole reaction. The visible irradiation was introduced into the reactor at the start of the reaction

Fig. 1. XRD patterns of CeO₂ (1), 0.05 PdO/CeO₂ (2), 0.1 PdO/CeO₂ (3), 0.5 PdO/CeO₂ (4), 1.0 PdO/CeO₂ (5), and 2.0 PdO/CeO₂ (6) samples.

time.

3. Results and discussion

3.1. Physical properties of CeO₂ and PdO/CeO₂

The XRD patterns of the as-prepared CeO₂ and PdO/CeO₂ powders are shown in Fig. 1. All the samples displayed the cubic CeO₂ (fluorite structure, JCPDS 34-0349). No Pd-related signals were seen in the spectra. The average crystal sizes of the samples are ca. 17–18 nm according to the Scherrer equation, based on the (111) reflection of CeO₂ [25]. Table 1 lists the average crystal sizes, specific surface areas, and pore volumes of the CeO₂ and PdO-CeO₂ powders. All samples have similar specific surface areas and pore volumes. This shows that PdO deposition has caused only small differences in the physical properties of the CeO₂. Consequently, the crystal size and specific surface area cannot be a basis for any possible variation of their catalytic performances.

The morphologies of CeO₂ and Pd/CeO₂ were observed with HRTEM. As shown in Fig. 2, CeO₂ has a grain size of ca. 15 nm, which is consistent with the XRD results. The interplanar spacing (*d*) was 0.27 nm, which corresponds to the (200) planes of the cubic cell of CeO₂ [14]. In the HRTEM images of 1.0 PdO/CeO₂ and 2.0 PdO/CeO₂, some smaller grains of ca. 5 nm appear and have an interplanar spacing of 0.28 nm, which fits the (200) planes of the cubic cell of PdO (JCPDS 46-1211).

Table 1

Physical parameters of the CeO₂ and PdO-CeO₂ catalysts.

Sample	<i>d</i> ^a (nm)	<i>A</i> _{BET} ^b (m ² /g)	Pore volume ^b (cm ³ /g)
CeO ₂	17.6	57.5	0.12
0.05 PdO/CeO ₂	17.1	55.6	0.12
0.1 PdO/CeO ₂	17.3	57.0	0.13
0.5 PdO/CeO ₂	17.7	57.6	0.13
1.0 PdO/CeO ₂	17.7	61.3	0.12
2.0 PdO/CeO ₂	16.4	58.6	0.17

^a Average crystallite size of CeO₂(111) according to the Scherrer equation.

^b Calculated from the N₂ adsorption-desorption isotherm.

3.2. Chemical states of the PdO/CeO₂ catalysts

Generally, the chemical states, especially the surface chemical states, of CeO₂ play an important role on the Ce³⁺/Ce⁴⁺ redox cycle and significantly affect the catalytic activity. Therefore, the chemical states of the PdO/CeO₂ were investigated by Raman and XPS spectra.

3.2.1. Raman results

The Raman spectra of the as-prepared catalysts (Fig. 3) were examined to investigate the oxygen vacancies in the CeO₂ [26–29]. The strong peak at 463 cm⁻¹ is due to an *F*_{2g} vibrational in a cubic fluorite lattice [10,29,30], while the bands around 593 cm⁻¹ and below 300 cm⁻¹ have been attributed to defect-induced modes [20,23,26,28]. It is known that the oxygen vacancy in CeO₂ is closely related to the presence of Ce³⁺ and thus is vital to the CeO₂/H₂O₂ catalytic system [18,20,23]. Practically, the concentration of oxygen vacancy in CeO₂ can be estimated by the ratio of the Raman peak intensity at 593 cm⁻¹ to that at 463 cm⁻¹, that is *I*₅₉₃/*I*₄₆₃. The *I*₅₉₃/*I*₄₆₃ values of the CeO₂ and PdO/CeO₂ powders are presented in Fig. 3(b). The PdO loading gradually increases *I*₅₉₃/*I*₄₆₃ from CeO₂ to 2.0 PdO/CeO₂. This increase in the *I*₅₉₃/*I*₄₆₃ ratio implies increased amounts of PdO enhances the oxygen vacancy levels in CeO₂.

In addition, a slight peak appears at 834 cm⁻¹ for PdO/CeO₂, which has been assigned to the stretching vibration of a peroxide-like (O₂²⁻) species [10,29]. The increased intensity at 834 cm⁻¹ suggests that the formation of surface peroxide-like species is also promoted by increased PdO loading, which in turn increases the amount of oxygen vacancy in CeO₂, and finally contributes to increase the Fenton-like reactivity of these PdO/CeO₂ composites.

Fig. 2. HRTEM images of CeO₂ (a), 1.0 PdO/CeO₂ (b), and 2.0 PdO/CeO₂ (c) samples.

Fig. 3. (a) Raman spectra of CeO₂ (1), 0.05 PdO/CeO₂ (2), 0.1 PdO/CeO₂ (3), 0.5 PdO/CeO₂ (4), 1.0 PdO/CeO₂ (5), and 2.0 PdO/CeO₂ (6); (b) Their corresponding I_{593}/I_{463} ratios.

3.2.2. XPS results

The surface chemical compositions of the CeO₂ and PdO-CeO₂ (Fig. 4) were further investigated with XPS spectroscopy. Figure 4(a) presents the fine XPS spectra of Pd 3d. Although the Pd 3d signals can hardly be observed at the lower Pd contents, they are suitably intense at higher contents. As shown in Fig. 4(a), two characteristic peaks were observed for the PdO/CeO₂ powders with a Pd content higher than 0.5 at%. According to the Ref. [7], the peaks at 343 and 338 eV correspond to the 3d_{3/2} and 3d_{5/2} signals of Pd²⁺ species, respectively. The 3d_{3/2} and 3d_{5/2} signals for metallic Pd⁰, which appear at 335.3 and 340.2 eV, respectively, were not observed in any of the PdO/CeO₂ samples. The chemical stability of Pd species was also observed by re-measuring the XPS after the Fenton-like reaction for the degradation of A07, where the same Pd²⁺ signals were observed.

Figure 4(b) shows the Ce 3d fine XPS spectrum of CeO₂ and its corresponding deconvolution peaks. The deconvolution of Ce 3d spectrum has been labeled as two pairs of doublets (v₀/u₀ and v'/u') assigned to Ce³⁺ and three pairs of doublets (v/u, v''/u'' and v'''/u''') assigned to Ce⁴⁺, in which vⁿ and uⁿ refer to the 3d_{5/2} and 3d_{3/2} spin-orbit components, respectively [30–32]. The relative concentration of Ce³⁺ in the catalysts could be obtained by calculating the relative areas under the

curve of each deconvoluted peak according to Eq. (1) [18,20,23,33,34]:

$$[\text{Ce}^{3+}] = \frac{(A_{v'} + A_{v_0} + A_{u'} + A_{u_0})}{(A_{v'''} + A_{v'} + A_{v''} + A_{v'''} + A_{u'''} + A_{u''} + A_{u'} + A_{u'''} + A_{u_0})} \quad (1)$$

in which A_i is the integration area of peak i .

Figure 4(c) presents the calculated relative concentrations of Ce³⁺ in the CeO₂ and PdO/CeO₂ powders. The concentration of Ce³⁺ in CeO₂ is 24.6%, less than in the PdO-deposited CeO₂, which were 25.5%, 26.4%, 27.8%, 28.4% and 26.4% for 0.05 PdO/CeO₂, 0.1 PdO/CeO₂, 0.5 PdO/CeO₂, 1.0 PdO/CeO₂, and 2.0 PdO/CeO₂, respectively. The PdO loading appears to have a direct effect on the chemical state of cerium ion in CeO₂. The relative concentration of Ce³⁺ increases with increasing PdO loading, with a slight decrease at a PdO loading of 2.0 at%.

The XPS and the Raman results reveal that the concentrations of Ce³⁺ and the oxygen vacancy gradually increase with increased amounts of PdO. The enhanced Ce³⁺ (and the associated oxygen vacancy) content in the catalyst should significantly promote the redox catalytic performance of PdO/CeO₂ [14]. By analogy, its activity of catalyzing H₂O₂ in the oxidation of organics should also be promoted.

3.3. Effect of PdO loading on the Fenton-like reactivity of CeO₂

The degradation of A07 and SA was employed to evaluate

Fig. 4. (a) XPS fine spectra of Pd 3d for CeO₂ (1), 0.05 PdO/CeO₂ (2), 0.1 PdO/CeO₂ (3), 0.5 PdO/CeO₂ (4), 1.0 PdO/CeO₂ (5), 1.0 PdO/CeO₂ after the Fenton-like reaction (6), and 2.0 PdO/CeO₂ (7); (b) XPS spectrum of Ce 3d for CeO₂; (c) Ce³⁺ content in various PdO/CeO₂ catalysts.

the Fenton-like reactivity of the $\text{CeO}_2/\text{H}_2\text{O}_2$ system. Figure 5 shows the Fenton-like degradation of A07 in the dark and under visible light irradiation with various catalysts. To avoid any interference due to A07 desorption, all reactions were carried out in a pre-mixed mode [19], i.e., CeO_2 was first mixed with H_2O_2 before the addition of the organic substances.

As shown in Fig. 5, the Fenton-like degradation of A07 was well fitted by first order kinetics. The corresponding degradation rate constants of A07 of the CeO_2 and $\text{PdO}-\text{CeO}_2$ catalysts are listed in Table 2. Figure 5(a) shows the Fenton-like degradation of A07 in the dark. The PdO loading obviously promoted the Fenton-like reactivity of the catalysts. The catalytic activity of the PdO/CeO_2 increases with increased PdO loading and reaches a maximum at a loading of 1.0 at%. The Fenton-like reactivity rate constant of 1.0 PdO/CeO_2 is 7.8-fold that of CeO_2 in this reaction. The catalytic activity correlates with the Ce^{3+} concentration in the catalysts. Previous work suggests that the catalytic action of the $\text{CeO}_2/\text{H}_2\text{O}_2$ system is mostly centered on the surface Ce^{3+} sites [35]. This Fenton-like degradation of A07 gives additional support to the surface Ce^{3+} site centered proposal for the $\text{CeO}_2/\text{H}_2\text{O}_2$ system.

Figure 5(b) shows the photo-Fenton-like degradation of A07 under visible irradiation. Under irradiation, the adsorbed A07 can be excited by visible photons and inject an electron into the CeO_2 . Our previous work [17,18,23] suggested that the injected electron would be trapped by interfacial peroxide-like species on the CeO_2 , which would initiate an intramolecular

Table 2

The degradation rate constants (k) of A07 of the CeO_2 and $\text{PdO}-\text{CeO}_2$ catalysts.

Sample	k/h^{-1}	
	In the dark	Under visible irradiation
CeO_2	0.078	0.798
0.05 PdO/CeO_2	0.119	1.65
0.1 PdO/CeO_2	0.143	1.76
0.5 PdO/CeO_2	0.365	2.80
1.0 PdO/CeO_2	0.606	3.90
2.0 PdO/CeO_2	0.585	3.69

rearrangement, and result in the release of free Ce^{3+} along with the produce of an $\cdot\text{OH}$ radical (Eq. (2)). As free Ce^{3+} and an $\cdot\text{OH}$ radical improve the Fenton-like reactivity, the degradation of A07 is greatly accelerated by visible irradiation.

The rate constants of the visible light assisted photo-Fenton-like degradation of A07 with the CeO_2 and $\text{PdO}-\text{CeO}_2$ catalysts are obviously higher than that without visible light irradiation. 1.0 PdO/CeO_2 also exhibits the highest visible light assisted photo Fenton-like reactivity among the catalysts described here. The introduction of visible irradiation increases the A07 degradation rate constants by 10.2 and 6.4 times with CeO_2 and 1.0 PdO/CeO_2 , respectively. Notably, the combined effects of PdO loading and visible light irradiation accelerate the Fenton-like degradation of A07 to ca. 50 times that of CeO_2 . It has been reported that the strong interaction between PdO and CeO_2 would induce the generation of oxygen vacancies and Ce^{3+} as well in the CeO_2 , while dye sensitization accelerates the Ce^{3+} regeneration through interfacial peroxides species by interfacial electron injection [14]. As a Ce^{3+} site-centered interfacial reaction, the degradation of A07 is thus greatly promoted.

A colorless chemical, SA, was also employed to evaluate the Fenton-like catalytic activity of PdO/CeO_2 . Figure 6 shows the Fenton-like degradation of SA with CeO_2 and $\text{PdO}-\text{CeO}_2$ catalysts in the dark and under visible irradiation. The corresponding Fenton-like degradation rate constants of SA are listed in Table 3. The PdO loading also affects the degradation rate of SA, and PdO/CeO_2 with a PdO loading of 1.0 at% exhibits the highest catalytic activity in either case. However, the magnitude of the improvement is smaller than that for the Fenton-like degradation of A07. Figure 6(b) shows the photo Fenton-like degradation of SA under visible irradiation. It seems that the introduction of visible irradiation has no effect on the Fenton-like degradation of SA. Since SA is a colorless substance, it is incapable of absorbing the visible photons and therefore does not help the Fenton-like degradation of SA in the $\text{CeO}_2/\text{H}_2\text{O}_2$ system.

Unexpectedly, the catalytic activity of PdO/CeO_2 for the degradation of SA decreases at low PdO loadings as the PdO loading increases, which was not seen for the degradation of A07. At higher PdO loading, the catalytic activity of PdO/CeO_2 increases to a maximum at 1.0 at%. The catalytic improvement by PdO loading is mainly attributed to the higher concentration of surface Ce^{3+} and additional interfacial peroxide species. However, according to our previous work [18–20,23], the CeO_2 -based Fenton-like degradation of organics occurs via an

Fig. 5. Fenton-like degradation of A07 with CeO_2 (1), 0.05 PdO/CeO_2 (2), 0.1 PdO/CeO_2 (3), 0.5 PdO/CeO_2 (4), 1.0 PdO/CeO_2 (5), and 2.0 PdO/CeO_2 (6). (a) In the dark; (b) Under visible light irradiation.

Fig. 6. Fenton-like degradation of SA with CeO_2 (1), 0.05 PdO/CeO_2 (2), 0.1 PdO/CeO_2 (3), 0.5 PdO/CeO_2 (4), 1.0 PdO/CeO_2 (5), and 2.0 PdO/CeO_2 (6). (a) In the dark; (b) Under visible irradiation.

Table 3

The degradation rate constants of SA of the CeO_2 and PdO/CeO_2 catalysts.

Sample	k/h^{-1}	
	In the dark	Under visible irradiation
CeO_2	0.043	0.044
0.05 PdO/CeO_2	0.037	0.038
0.1 PdO/CeO_2	0.029	0.029
0.5 PdO/CeO_2	0.056	0.057
1.0 PdO/CeO_2	0.083	0.080
2.0 PdO/CeO_2	0.077	0.077

interfacial reaction, and is an adsorption-triggered process; therefore, the adsorbability of the CeO_2 should also affect the Fenton-like reactivity.

The adsorption rates of AO7 and SA are presented in Fig. 7. To avoid the possible interference from competitive adsorption by H_2O_2 , the adsorption rates were measured according to the following procedure. An AO7 (or SA) solution was mixed with the corresponding catalyst in the dark for 1.0 h to achieve a pre-adsorption. Then, the required amount of H_2O_2 solution was quickly added to reach a concentration of 20 mmol/L. After stirring for 2 min and centrifuging to remove the catalyst, the concentration of AO7 (or SA) was measured to estimate the adsorption rate of the organic material.

Figure 7 shows that AO7 adsorbs well on the CeO_2 and gives an adsorption rate of ca. 50%. The PdO loading does not significantly affect the adsorbability of the catalysts. However, the

Fig. 7. Adsorption of AO7 (35 mg/L) and SA (20 mg/L) onto the various catalysts.

adsorption of SA on CeO_2 is significantly weaker than for AO7, which gives an adsorption rate of 13% on CeO_2 . The PdO loading further reduces this at lower concentrations. As shown in Fig. 7, there are only 7% and 3% of SA molecules adsorbed on the 0.05 PdO/CeO_2 and 0.1 PdO/CeO_2 , respectively. Beyond this, the adsorption increases to close to the initial value. As the Fenton-like degradation of organic material based on $\text{CeO}_2/\text{H}_2\text{O}_2$ is an interfacial reaction, the degradation kinetics of the organic material depends on its adsorption onto the surface of CeO_2 . At low PdO contents (less than the 0.5 at%), the deposited PdO on the surface of CeO_2 occupies the SA adsorption sites, thus decreasing the ability of the catalysts to adsorb SA and this decreases the catalytic activity. As the PdO content increases further, the adsorption of SA on the catalysts is restored. Simultaneously, as the interaction between PdO and CeO_2 increases, the Ce^{3+} content in the CeO_2 increases. The Fenton-like degradation of SA is significantly accelerated, reaching a maximum at the PdO loading of 1.0 at%.

4. Conclusions

PdO/CeO_2 catalysts were prepared by deposition-precipitation method. The PdO/CeO_2 composites have a cubic CeO_2 structure, ca. 17 nm in diameter and have similar specific surface areas with that of bare CeO_2 . The Pd in the composites is present as Pd^{2+} , and the deposited PdO particles are ca. 5 nm in size. The introduction of PdO increases the relative concentration of Ce^{3+} in CeO_2 . Deposition of PdO accelerates the Fenton-like degradation of SA, with a maximum rate at the PdO loading of 1.0 at%. For AO7, a dye sensitization effect was observed under the visible irradiation, which accelerates the regeneration of Ce^{3+} from interfacial peroxides species by interfacial electron injection from an excited AO7 molecule to the CeO_2 catalyst. The Fenton-like degradation rate constant of AO7 with bare CeO_2 in dark is 0.078 h^{-1} , while that with 1.0 PdO/CeO_2 increases to 3.9 h^{-1} under visible irradiation, a 50-fold improvement.

Graphical Abstract

Chin. J. Catal., 2015, 36: 314–321 doi: 10.1016/S1872-2067(14)60261-8

The enhanced Fenton-like catalytic performance of PdO/CeO₂ for the degradations of acid orange 7 and salicylic acid

Lin Ge, Chengjie Zang, Feng Chen*

East China University of Science and Technology

Deposited PdO nanoclusters promote the regeneration of Ce³⁺ by interfacial peroxide species on the surface of CeO₂ and therefore enhance the Fenton-like degradation of AO7 both in the dark and under visible irradiation.

References

- [1] Trovarelli A, de Leitenburg C, Boaro M, Dolcetti G. *Catal Today*, 1999, 50: 353
- [2] Sun C W, Li H, Chen L Q. *Energy Environ Sci*, 2012, 5: 8475
- [3] Besson M, Descorme C, Bernardi M, Gallezot P, di Gregorio F, Grosjean N, Pham Minh D, Pintar A. *Environ Technol*, 2010, 31: 1441
- [4] Singh P, Hegde M S. *Chem Mater*, 2009, 21: 3337
- [5] Nolan M. *J Phys Chem C*, 2011, 115: 6671
- [6] Tanaka A, Hashimoto K, Kominami H. *J Am Chem Soc*, 2012, 134: 14526
- [7] Hinokuma S, Fujii H, Okamoto M, Ikeue K, Machida M. *Chem Mater*, 2010, 22: 6183
- [8] Liu X Y, Liu M H, Luo Y C, Mou C Y, Lin S D, Cheng H K, Chen J M, Lee J F, Lin T S. *J Am Chem Soc*, 2012, 134: 10251
- [9] Gnanamani M K, Jacobs G, Shafer W D, Ribeiro M C, Pendyala V R, Ma W P, Davis B H. *Catal Commun*, 2012, 25: 12
- [10] Guzman J, Carrettin S, Corma A. *J Am Chem Soc*, 2005, 127: 3286
- [11] Zhou H P, Wu H S, Shen J, Yin A X, Sun L D, Yan C H. *J Am Chem Soc*, 2010, 132: 4998
- [12] Wieder N L, Cargnello M, Bakhmutsky K, Montini T, Fornasiero P, Gorte R J. *J Phys Chem C*, 2011, 115: 915
- [13] Shen W J, Ichihashi Y, Okumura M, Matsumura Y. *Catal Lett*, 2000, 64: 23
- [14] Meng L, Jia A P, Lu J Q, Luo L F, Huang W X, Luo M F. *J Phys Chem C*, 2011, 115: 19789
- [15] Colussi S, Gayen A, Camellone F M, Boaro M, Llorca J, Fabris S, Trovarelli A. *Angew Chem Int Ed*, 2009, 48: 8481
- [16] Heckert E G, Seal S, Self W T. *Environ Sci Technol*, 2008, 42: 5014
- [17] Ji P F, Tian B Z, Chen F, Zhang J L. *Environ Technol*, 2012, 33: 467
- [18] Cai W D, Chen F, Shen X X, Chen L J, Zhang J L. *Appl Catal B*, 2010, 101: 160
- [19] Chen F, Shen X X, Wang Y C, Zhang J L. *Appl Catal B*, 2012, 121: 223
- [20] Wang Y C, Shen X X, Chen F. *J Mol Catal A*, 2014, 381: 38
- [21] Ji P F, Zhang J L, Chen F, Anpo M. *Appl Catal B*, 2009, 85: 148
- [22] Chen F, Shen X X. *Appl Catal B*, 2011, 105: 252
- [23] Ge L, Chen T, Liu Z Q, Chen F. *Catal Today*, 2014, 224: 209
- [24] Xiao L H, Sun K P, Xu X L, Li X N. *Catal Commun*, 2005, 6: 796
- [25] Carrettin S, Concepción P, Corma A, López Nieto J M, Puentes V F. *Angew Chem Int Ed*, 2004, 43: 2538
- [26] Lee Y, He G, Akey A J, Si R, Flytzani-Stephanopoulos M, Herman I P. *J Am Chem Soc*, 2011, 133: 12952
- [27] McBride J R, Hass K C, Poindexter B D, Weber W H. *J Appl Phys*, 1994, 76: 2435
- [28] Orge C A, Órfão J J M, Pereira M F R, Duarte de Farias A M, Neto R C R, Fraga M A. *Appl Catal B*, 2011, 103: 190
- [29] Pushkarev V V, Kovalchuk V I, d'Itri J L. *J Phys Chem B*, 2004, 108: 5341
- [30] Bêche E, Charvin P, Perarnau D, Abanades S, Flamant G. *Surf Interf Anal*, 2008, 40: 264
- [31] Holgado J P, Alvarez R, Munuera G. *Appl Surf Sci*, 2000, 161: 301
- [32] Tsunekawa S, Fukuda T, Kasuya A. *Appl Surf Sci*, 2000, 157: 1437
- [33] Korsvik C, Patil S, Seal S, Self W T. *Chem Commun*, 2007: 1056
- [34] Watanabe S, Ma X, Song C. *J Phys Chem C*, 2009, 113: 14249
- [35] Ji P F, Wang L Z, Chen F, Zhang J L. *ChemCatChem*, 2010, 2: 1552

PdO/CeO₂类芬顿降解酸性橙7和水杨酸的催化性能

葛琳, 臧成杰, 陈锋*

华东理工大学结构可控先进功能材料及其制备教育部重点实验室, 精细化工研究所, 上海200237

摘要: 采用沉淀-沉积法制备了PdO/CeO₂催化剂, 并使用X射线衍射、高分辨透射电镜、N₂吸附-脱附等温线、X射线光电子能谱和Raman光谱对催化剂进行了表征。表征结果显示, Pd在复合物中以Pd²⁺形式存在; PdO和CeO₂间的相互作用提高了CeO₂中的

Ce³⁺含量. 通过酸性橙7和水杨酸的类芬顿降解考察了PdO/CeO₂的多相类芬顿和可见光芬顿催化活性. 结果表明, PdO沉积显著地促进了水杨酸的类芬顿降解, 催化剂的PdO含量为1.0 at%时其活性最佳. 染料酸性橙7在可见光照射条件下会引发染料光敏化效应. 吸附的染料分子在光激发后通过界面电子注入促进了Ce³⁺自表面过氧物种的再生. 由此, PdO负载和可见光照射的共同作用下, 1.0 PdO/CeO₂催化剂的酸性橙7类芬顿降解速率常数为3.90 h⁻¹, 为纯CeO₂活性的50倍左右.

关键词: 类芬顿反应; 二氧化铈; 氧化钯; 降解; 过氧化氢

收稿日期: 2014-10-21. 接受日期: 2014-12-01. 出版日期: 2015-03-20.

*通讯联系人. 电话: (021)64253056; 电子信箱: fengchen@ecust.edu.cn

基金来源: 国家自然科学基金(21177039); 上海市教委科研创新项目(13ZZ042).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

《催化学报》为被国际期刊退稿的高质量论文开辟绿色通道

我们注意到, 国内一些高质量、原创性的研究工作在投稿到国际期刊上时, 经常因语言和写作问题等非科学因素而被退稿和拖延发表, 甚至会失去原创知识产权, 这个损失是巨大的, 也是非常可惜的!

众所周知, 按国际学术界的共识, 获得论文的首发权并保证拥有研究工作的原创性不在于论文发表在哪个刊物(只要是国际ISSN挂号的), 而在于谁第一时间抢先发表了工作.

为了保护作者工作的原创性和首发知识产权, 《催化学报》编委会决定为具有一定原创性的论文提供快速发表的绿色通道. 对于投到国际著名期刊(如Science, Nature, Energy & Environmental Science, Journal of the American Chemical Society, Angewandte Chemie International Edition, ACS Catalysis和Journal of Catalysis等)上催化论文的退稿, 如果其创新性较强, 学术质量较高, 仅仅是因为语言和文章写作原因而被退稿, 《催化学报》会安排其在最近一期上抢时间发表; 如果文章原创性较好, 不存在学风问题, 但有一些理论观点的争议、实验现象暂时无法得到完美的理论解释, 或者需要进一步补充相关实验数据等, 本刊主编、副主编也会协助作者尽快修改和发表相关工作.

对于国际著名相关期刊的退稿, 作者需将相应的审稿意见及意见答复等材料一并提交到本刊, 以加快论文的处理速度.