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Efficient degradation of pyruvic acid in water by catalytic ozonation with PdO/CeO_2

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ABSTRACT

PdO/CeO_2 prepared at various calcination temperatures and Pd loading percentages significantly enhanced the degradation of pyruvic acid (PA) in water by catalytic ozonation compared to ozonation alone. The surface property of PdO/CeO_2 was characterized with X-ray diffraction, transmission electron microscope, X-ray photoelectron spectroscopy, BET surface area and zeta potential, and its relationship with the catalytic activity was examined and discussed in detail. Results indicate that PdO/CeO_2 with 4.0% of Pd loading and calcined at 550 °C showed the highest catalytic activity in PA degradation by ozone. Complete PA ($5\,mg\,L^{-1}$) removal was quickly achieved in catalytic ozonation at 5 min and pH 4.7, in which PdO and CeO_2 exerted a synergic effect. Moreover, PdO/CeO_2 exhibited a persistently high activity throughout the semi-continuous ozonation of PA. It was observed that the surface contents of Ce(III) and Pd(II) were closely related to the catalytic activity and the optimal surface molar ratio of Ce(III)/Pd(II) was around 1:1. The positively charged surface of PdO/CeO_2 also played an important role in catalyzing PA degradation by ozone.

1. Introduction

Ozonation has been widely used for organic pollutants removal from water and wastewater. Ozone is reactive towards many organic pollutants, especially those containing aromatic rings, double bonds, and amine- or sulfur-moieties [1,2]. However, the reaction rates between ozone and a significant amount of other organic pollutants are rather low, making them difficult to degrade during ozonation. Among these organics, ozonation by-products such as small carboxylic acids, ketones and aldehydes are hardly reactive to ozone [3,4]. Pyruvic acid (PA), a major by-product formed during the ozonation of water containing dissolved aromatic compounds or natural organic matter, is quite resistant to further oxidation by ozone ($k = 0.025\,min^{-1}$) [5]. Thus, heterogeneous catalytic ozonation has been studied to promote the oxidation of PA in recent years. It was reported that Co/Al_2O_3 [6], MnO_2 and Mn^{2+} ions [7], $CuO/ZrO_2–Al_2O_3$ [8], perovskite ($LaTi_{0.15}Cu_{0.85}O_3$) [9] and activated carbon [5] could catalyze PA degradation by ozone. However, most of these works focused on the influence of experimental conditions (e.g., pH, ozone dose, contact time) on PA removal while the relationship between the surface property and catalytic activity of the studied catalysts was much less concerned. Alvarez et al. [6] investigated the structural characteristics of Co/Al_2O_3 used for the catalytic ozonation of PA and found that the different surface Co phases showed different catalytic activities. The catalyst with Co_3O_4 as the main Co phase was the most active, achieving about 28% removal of PA at 20 min and pH 2.5 in catalytic ozonation.

In this study, we found that PdO/CeO_2 prepared at various calcination temperatures and Pd loadings was efficient in promoting the degradation of PA by ozone at elevated pH values (i.e., pH 4.7–6.0), which may favor its application in water treatment. In addition, through detailed examination of the property–activity relationship, the important surface properties governing the catalytic activity of PdO/CeO_2 were proposed.

2. Experimental

2.1. Catalyst preparation

CeO_2 was synthesized by urea-hydrothermal means with certain modification [10]. Specifically, $Ce(NO_3)_3·6H_2O$ and urea were co-dissolved in distilled water with a molar ratio of 1:3. The mixture was then transferred to a sealed stainless steel vessel and heated at 140 °C for 5 h. After filtration and repeated washings, the precipitate was dried at 120 °C for 2 h and calcined at 450 °C for 4 h. The diameter of CeO_2 particles was mainly in the range of 0.6–7.7 μm.

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PdO/CeO_2 was prepared by impregnating CeO_2 with $Pd(NO_3)_2$ aqueous solution according to the incipient wetness method with some modification [11]. The calculated Pd content (wt.%) loaded on the catalyst ranged from 0.6% to 4.7%. The impregnated samples were dried at 60 °C and finally calcined in air for 3 h at temperatures ranging from 400 to 800 °C. The heating rate was 2 °C min^{-1} in all calcinations. The prepared catalysts were designated as PdO/CeO_2-*X*%-*Y*°C, where *X* refers to the weight percentage of Pd and *Y* to the calcination temperature.

2.2. Catalyst characterization

The morphology of catalysts was visualized using transmission electron microscope (TEM) (H-7500, Hitachi, Japan). The BET surface area was determined by adsorption and desorption of N_2 on a Micromeritics ASAP2000 analyzer. X-ray powder diffraction (XRD) measurement was carried out using a Bruker D8 Advance X-diffractometer (Cu Kα, λ = 0.15406 nm). The surface molar percentages of Pd and Ce were determined by X-ray photoelectron spectroscopy (XPS) with an Escalab 250 spectrometer (Thermofisher), and the XPS data corresponding to Ce 3d and Pd 3d spectra were fitted with Peakfit software (V4.12). The molar percentages of Ce and Pd of different valences with respect to the total Ce and Pd, respectively, were also analyzed from the XPS data. Zeta potential was determined by a Malvern zetameter (2000, Zetasizer). The particle size was measured with a laser particle size analyzer (2000, Mastersizer) in water.

2.3. Experimental procedures

Experiments were conducted in a 1-L cylindrical glass reactor with temperature controlled at 22 °C under magnetic agitation. The reactor was installed with an inlet and an outlet for ozone gas and sampling accessories. In a typical experiment, 500 mL aqueous suspension of PA (buffered with 10 mM borate) and 0.15 g catalyst were added into the reactor. Ozone, generated from dried oxygen with an ozone generator (3S-A5, Tonglin Technology, Beijing), was continuously bubbled into the reactor at a flow rate of 4 L min^{-1} and a gaseous concentration of 1.4 mg L^{-1}. Aqueous ozone concentration was determined with the indigo method [12]. Samples withdrawn at specific time intervals were filtered with 0.45-μm synthetic fiber filters after the residual ozone had been immediately quenched by Na_2SO_3. PA was analyzed on a high-performance liquid chromatograph (HPLC) (1200, Agilent) equipped with an Atlantis dC18 column and a UV detector at 215 nm. The mobile phase (0.8 mL min^{-1}) was a mixture of 10 mM NaH_2PO_4 solution (adjusted to pH 2.8) and methanol (V:V = 95:5).

3. Results

3.1. Catalyst characterization

3.1.1. Catalyst structure

The XRD patterns of CeO_2 and PdO/CeO_2 catalysts prepared in this work are shown in Fig. 1. PdO/CeO_2 with different Pd loadings calcined at temperatures no higher than 550 °C showed a characteristic cubic fluorite structure of CeO_2. When the calcination temperature was raised up to 650 °C and especially 800 °C, a peak at $2\theta = 33.9°$ emerged that is typical for the (1 0 1) diffraction of PdO [13]. The result indicates that PdO was well dispersed on the CeO_2 surface at lower calcination temperatures, while agglomerated at higher temperatures. With the Scherrer formula [14], the crystallite sizes of the catalysts were calculated to be within the range of 9.0–12.8 nm.

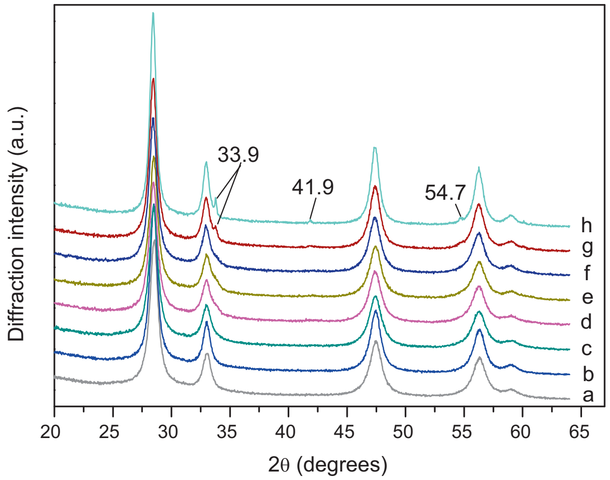

Fig. 1. XRD patterns of CeO_2 and PdO/CeO_2: (a) CeO_2; (b) PdO/CeO_2-0.6%-400 °C; (c) PdO/CeO_2-1.8%-400 °C; (d) PdO/CeO_2-4.0%-400 °C; (e) PdO/CeO_2-4.7%-400 °C; (f) PdO/CeO_2-4.0%-550 °C; (g) PdO/CeO_2-4.0%-650 °C; and (h) PdO/CeO_2-4.0%-800 °C.

The TEM picture (Fig. 2A) shows that CeO_2 mainly existed in the form of nanorods. The catalysts with Pd loadings from 1.8% to 4.7% maintained the nanorods form (Figs. 2B–D). The PdO/CeO_2 particles appeared somewhat larger than CeO_2, possibly due to the uniform deposition of PdO. Unlike the PdO/CeO_2 calcined at relatively lower temperatures such as 550 °C (Fig. 2E), the one calcined at 800 °C showed an obvious crystallite agglomeration, forming irregular-shaped particles (Fig. 2F).

3.1.2. Surface elemental composition and BET surface area

Table 1 shows the surface molar percentages of Ce and Pd and the BET surface areas of PdO/CeO_2 prepared at various calcination temperatures and Pd loadings. The surface molar percentage of Ce gradually increased as the calcination temperature increased from 400 to 800 °C, whereas that of Pd generally decreased, which was probably ascribed to the release of lattice oxygen from CeO_2 and the clustering of PdO particles. Calcination at temperatures higher than 550 °C led to a significant decrease in the BET surface area, which could also be attributed to the particle clustering as shown in the TEM picture (Fig. 2F). However, the BET surface area was almost independent of the Pd loading in the studied range of 0.6–4.7%.

Table 1
Surface elemental compositions and BET surface areas of CeO_2 and PdO/CeO_2.

Catalysts	Ce (at.%)	Pd (at.%)	Ce/Pd	BET surface area ($m^2\ g^{-1}$)
CeO_2	10.5			108
PdO/CeO_2-4.0%-400 °C	7.5	4.7	1.6	90
PdO/CeO_2-4.0%-550 °C	8.0	5.4	1.5	94
PdO/CeO_2-4.0%-650 °C	9.7	3.7	2.6	80
PdO/CeO_2-4.0%-800 °C	10.4	3.0	3.4	51
PdO/CeO_2-0.6%-400 °C	10.6	1.2	8.6	90
PdO/CeO_2-1.8%-400 °C	9.2	2.6	3.5	95
PdO/CeO_2-4.7%-400 °C	6.7	9.3	0.7	92

3.2. Catalytic ozonation of PA with PdO/CeO_2

3.2.1. Influence of calcination temperature

Only 26% of PA was degraded in ozonation alone at pH 4.7 at 20 min (Fig. 3A). The presence of PdO/CeO_2 significantly promoted PA degradation and the catalysts calcined at lower temperatures (e.g., 400 and 550 °C) were more active. The highest PA degradation rate (e.g., 100% removal at 5 min) was observed for PdO/CeO_2 calcined at 550 °C, which was slightly higher than that for PdO/CeO_2 calcined at 400 °C (e.g., 99% at 5 min). As the calcination temperature was further raised, the catalytic activity of PdO/CeO_2