Carbon-supported palladium catalysts for the direct synthesis of hydrogen peroxide from hydrogen and oxygen

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ABSTRACT

Twelve kinds of carbon materials were studied as supports of palladium catalysts for the direct synthesis of hydrogen peroxide. The correlation between the catalytic performance and the structure and physico-chemical properties of carbon materials suggested the important roles of the graphitic structure and the surface function groups in the selective formation of H_2O_2. The carbon material with a higher degree of graphitic structure and a lower density of surface COOH groups provided higher H_2O_2 selectivity and productivity. The chemical state and the mean size of Pd particles also affected the catalytic behavior. Metallic Pd was more efficient than PdO, and the catalyst with a smaller mean size of Pd nanoparticles exhibited higher activity and H_2O_2 selectivity. The presence of a mineral acid rather than a halide promoter and an organic solvent contributed to the selective formation of H_2O_2.

1. Introduction

Hydrogen peroxide (H_2O_2) is widely used in industrial processes such as chemical synthesis (e.g., propylene oxide production), pulp and paper bleaching, and waste treatment (e.g., Fenton process). The demand for H_2O_2 is growing rapidly in the chemical synthesis owing to its environmentally friendly character since H_2O is the only by-product. Currently, H_2O_2 is mainly produced by the anthraquinone process in the industry, which involves the sequential hydrogenation and oxidation of an alkyl anthraquinone. As compared to this high-cost and energy-intensive multi-step process, the direct synthesis of H_2O_2 from O_2 and H_2 by heterogeneous catalysis [Eq. (1)] is more desirable [1–4]. However, the direct synthesis of H_2O_2 is one of the biggest challenges in catalysis. Generally, H_2O_2 is difficult to obtain with high selectivity at a high H_2 conversion because of the following side reactions: (1) the oxidation of H_2 to H_2O [Eq. (2)], (2) the decomposition of H_2O_2 [Eq. (3)], and (3) the reduction of H_2O_2 by H_2 [Eq. (4)].

$$H_2 + O_2 \rightarrow H_2O_2 \qquad (1)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \qquad (2)$$

$$H_2O_2 \rightarrow H_2O + 1/2O_2 \qquad (3)$$

$$H_2O_2 + H_2 \rightarrow 2H_2O \qquad (4)$$

Only a few systems exhibit high efficiency for the direct synthesis of H_2O_2, although many papers have been published for the direct synthesis of H_2O_2 in the recent years [5–38]. The most extensively studied catalysts are supported palladium or palladium-based bimetallic catalysts. Besides the active phase, the support also plays key roles in determining the catalytic performance for H_2O_2 production. Several studies indicated that the carbon materials such as Aldrich G60 [18–20] and N-doped CNT [28,29] were more efficient supports for H_2O_2 formation than the conventional metal oxides such as SiO_2, Al_2O_3, TiO_2, and Fe_2O_3. Pd nanoparticles loaded on Vulcan XC-72 [11], a kind of carbon black, and on graphite [35] were found to be highly selective for the formation of H_2O_2. The catalytic behaviors of catalysts with different carbon supports varied distinctly [35]. However, the insights into the correlation between the structure and property of carbon supports and the catalytic performance are still lacking.

Carbon materials have been used in heterogeneous catalysis for a long time, showing unique performances as catalysts or catalyst supports [39–43]. However, the knowledge of the effects of the

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structures and properties of carbon materials on the catalytic performance is still insufficient. This is probably because of the high complexity of the structures and properties of carbon materials [39]. Depending on the synthetic methods and precursors, carbon atoms may take sp^3- and sp^2-structures in carbon materials, leading to various carbon allotropes such as diamond, graphite, nanofiber, nanotube, graphene, and fullerene. Moreover, amorphous, quasi-amorphous, and crystalline states of carbon may appear in different fractions in carbon blacks, activated carbons, cokes, soot, and glassy carbon, making the carbon materials irregular. Furthermore, the surface functional groups generated during the modification can also exert an influence on the properties of carbon materials [39,42,43]. In short, carbon materials exhibit variety in morphology, structures, and surface properties, and these make the establishment of structure–property and structure-performance relationships quite challenging.

To the best of our knowledge, there are no systematic studies focusing on the clarification of the effects of the structures and physicochemical properties of carbon supports toward their catalytic behaviors in the direct synthesis of H_2O_2. The main purpose of this paper was to report our detailed studies of Pd catalysts loaded on various kinds of carbon materials for the direct synthesis of H_2O_2. The carbon supports involved in our work include activated carbons, carbon blacks, graphite, carbon nanotube (CNT), and carbon nanofiber (CNF). The key factors determining the catalytic behavior for the formation of H_2O_2 such as the structure and surface properties of carbon supports, the chemical state and size of Pd particles, the solvent, and the presence of mineral acids will be discussed.

2. Experimental

2.1. Materials and catalyst preparation

Carbon materials used in this work were as follows: (1) graphite obtained from Shanghai Colloidal Chemical Plant; (2) VGCF (vapor-growing carbon fiber) from Showa Denko; (3) carbon blacks including XC (extra conduction) series (XC-72, XC-72R, and XC-605), ML (mogul L), BP-2000 (black pearls 2000) from Shanghai Cabot Chemical Co. Ltd., and U-CB (U-carbon black) from Shanghai Chemical Reagent Company Limited.; and (4) activated carbons including AC-WC (activated carbon from wood charcoal), AC-CS (activated carbon from coconut shell), and AC-NS (activated carbon from nut shell) from Shanghai Chemical Reagent Company Limited. Multi-walled CNTs with a herringbone structure were prepared by an established method [44]. The impurities contained in the carbon materials, which mainly included Fe, Cu, or Ni, were removed by pretreatment using 37 wt% HCl aqueous solution at room temperature for 2 days. The recovered carbon materials were then washed thoroughly with deionized water until no Cl^- remained, and then dried overnight at 393 K. To study the effect of the surface oxygen-containing functional groups on carbon materials, we also pretreated XC-72 by HNO_3 aqueous solutions with concentrations ranging from 2 to 68 wt% under refluxing conditions at 110 °C for 2 h. The pretreated XC-72 was recovered by centrifugation and then washed thoroughly with deionized water until pH = 7, followed by drying overnight at 393 K.

Pd catalysts loaded on various carbon materials as well as some typical metal oxides were prepared by a chemical reduction method using HCHO as a reductant. Acidic $PdCl_2$ aqueous solution with a Pd^{2+} concentration of 1.5 mg L^{-1} was used as the precursor of Pd. The carbon support was added into the aqueous solution of $PdCl_2$ containing an appropriate amount of ethanol to obtain a homogeneous distribution in $PdCl_2$ solution. Then, a 5.0 wt% HCHO aqueous solution with a pH at 7.0 was added into the suspension containing Pd^{2+} and the support. The molar ratio of $HCHO/Pd^{2+}$ was typically fixed at 2. The slurry was then kept under agitation at 60 °C for 0.5 h. The supported Pd catalysts were recovered by filtration, followed by washing with deionized water until the Cl^- ions could no longer be detected in the filtrate with a 1.0 M $AgNO_3$ aqueous solution. The catalysts were finally dried at 60 °C for 6 h before use.

For the sake of comparison, the conventional wet impregnation was also employed to prepare the supported Pd catalysts. In brief, a suspension containing the support and an acidic $PdCl_2$ aqueous solution was stirred for 8 h at room temperature, and then, water was evaporated at 90 °C. The dried solid powder was further treated in air at 300 °C for 1 h, followed by H_2 reduction at 300 °C for 1 h.

2.2. Catalyst characterization

The catalysts were characterized by various techniques. Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the loading of Pd in the catalysts with an Agilent ICP-MS 4500 instrument. Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to analyze the crystalline structure and the morphology of the catalysts. XRD patterns were collected on a Panalytical X'pert Pro diffractometer using Cu Kα radiation (40 kV, 30 mA). SEM measurements were taken on a Hitachi S-4800 operated at 15 kV. Laser Raman spectroscopic measurements, which were applied to analyze the graphitic structure of the carbon supports, were performed on a Renishaw 1000R Raman system. A green laser at 532 nm was used as the excitation source and the spectra were recorded in the range of 100–2000 cm^{-1}. N_2 physisorption was performed on an ASAP 2010 M Micromeritics apparatus to gain information about the surface area and the pore structure of each catalyst.

Transmission electron microscopy (TEM) was performed on a FEI Tecnai 30 electron microscope (Phillips Analytical) or a JEM 2100 electron microscope (JOEL) to gain information about the size of Pd particles. The chemisorption of CO was performed using a Micromeritics ASAP 2010C to measure the dispersion of Pd. The oxidation state of Pd was investigated by X-ray photoelectron spectroscopy (XPS) using a Quantum 2000 Scanning ESCA Microprob instrument (Physical Electronics) with Al Kα radiation source (1846.6 eV). The binding energy was calibrated using C1s photoelectron peak at 284.6 eV as a reference.

The Boehm titration method [45], in which the amounts of base uptake were measured by titration, was used to quantify the acidic functional groups on the surfaces of carbon materials. The bases used in this work included $NaHCO_3$ [pK($NaHCO_3$) = 6.37], Na_2CO_3 [pK(Na_2CO_3) = 10.25], and NaOH [pK(NaOH) = 15.74]. For a normal titration experiment, the sample was divided into three parts with each 1.0 g in weight and then was added in three separate airtight glass bottles containing 50 mL of 0.05 M $NaHCO_3$, Na_2CO_3, and NaOH solution. Subsequently, the bottles were gently shaken for 24 h, and the filtrates were separated from the suspension. The amount of each base adsorbed on the carbon material was determined by the back titration of the filtrate with 0.05 M HCl using 2–3 drops of phenolphthalein as indicator.

A mass titration technique was employed to determine the point of zero charge (PZC) of the carbon materials [45]. The measurement was taken using a 0.05 M NaCl aqueous solution as a background electrolyte. Three NaCl solutions with different initial pH values (3.0, 6.0, and 11) were prepared using 0.1 M HCl or 0.1 M NaOH solutions. Then, carbon materials with different masses (1.0–8.0 g) were added into the NaCl solutions with different pH values. The equilibrium pH value of each suspension was measured after 24 h under agitation at 25 °C. As the mass fraction of carbon in the solution increased, the equilibrium pH value