Journal of Catalysis 365 (2018) 125–137

Contents lists available at ScienceDirect

Journal of Catalysis

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

Direct synthesis of hydrogen peroxide over Pd/C catalyst prepared by selective adsorption deposition method

Seungsun Lee [a,1], Hwiram Jeong [b,1], Young-Min Chung [a,*]

[a] Department of Nano & Chemical Engineering, Kunsan National University, 558 Daehak-ro, Kunsan, Jeollabuk-Do 573-701, Republic of Korea
[b] Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea

ARTICLE INFO

Article history:
Received 27 April 2018
Revised 21 June 2018
Accepted 25 June 2018

Keywords:
Hydrogen peroxide
Pd/C
Selective adsorption deposition
Surface modification
Catalyst poisoning

ABSTRACT

A new catalyst design based on selective adsorption deposition method was developed to achieve high reaction performance in the direct synthesis of hydrogen peroxide. The activity of the unprecedented Pd/C catalyst was superior to that of the conventionally prepared Pd/C catalysts, and the initial H_2O_2 productivity and H_2 selectivity reached as high as 8606 mmol H_2O_2/g Pd.h and 95.1%, respectively. This excellent activity may result from the intrinsic structural and electronic features of the active sites, *i.e.*, the extremely small and monodispersed Pd nanoparticles with a high Pd^{2+}/Pd^0 ratio, which were realized by combining the selective adsorption of metal precursor cations on a negatively charged activated carbon surface and the subsequent homogeneous surface deposition of palladium hydroxide by the hydroxide ions that are slowly generated upon urea decomposition. The catalytic activity was significantly affected by the oxygen groups of the activated carbon support. The carboxyl groups do not efficiently suppress the unfavorable H-OOH dissociation but rather accelerate the H_2O_2 hydrolysis by forming hydrogen bonds with H_2O_2. Moreover, a sharp decrease in the reaction rates of H_2O_2 hydrogenation and direct synthesis of H_2O_2 was observed with the increase in the number of carboxyl groups on the activated carbon surface. This loss of activity, as confirmed by acid treatment and olefin hydrogenation experiments, implies that the carboxyl groups in close proximity to the active sites have a detrimental effect by hindering or poisoning the active sites.

1. Introduction

Hydrogen peroxide (H_2O_2) is one of the greenest and most important oxidants, with applications ranging from bleaching agents, detergents, disinfectants, and wastewater treatment agents to semiconductor purification solutions and liquid rocket propellants [1]. In the petrochemical industry, hydrogen peroxide has been used in a number of oxidation reactions including the epoxidation of propylene to propylene oxide [2,3]. Recently, it was also reported that hydrogen peroxide could be effectively used in the low temperature oxidation of methane to methanol [4–6]. As the decomposition or hydrogenation of H_2O_2 only produces water, hydrogen peroxide has attracted much attention from an environmental point of view in addition to its importance as an efficient oxidizing agent.

Despite its environmentally benign nature, most hydrogen peroxide production has relied on environmentally unfavorable routes; for instance, the anthraquinone process involves various energy-intensive steps, the use of toxic compounds, and troublesome separation processes that generate waste materials [1,7]. Furthermore, mass production of hydrogen peroxide and ensuing intensive concentration of up to 70 wt% are essential to ensure economic efficiency [8]. As several reactions require 2–10 wt% H_2O_2 as oxidant [9], and the transportation of highly concentrated hydrogen peroxide is potentially dangerous, there are strong needs for the development of an efficient process enabling the onsite production of H_2O_2 on a controllable scale [1,7,8,10].

In this context, the direct synthesis of hydrogen peroxide from hydrogen and oxygen has drawn considerable attention because hydrogen peroxide can in principle be produced through a simple reaction route without any byproducts, except for water. In line with the promising aspects of the reaction from an environmental as well as economic viewpoint, the last decade witnessed a number of studies focusing on realizing unique and sophisticated catalyst designs [1,7,10]. For example, a number of novel approaches have been envisaged: (i) fine tuning of active metal properties by bimetal formation [11–18], phase control [19–23], or ligand capping [24]; (ii) suppression of side reactions by adopting core-shell

* Corresponding author.
E-mail address: ymchung@kunsan.ac.kr (Y.-M. Chung).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.jcat.2018.06.024
0021-9517/

structures [25,26], carbon diffusion coating layers [27], as well as solid acid supports [28–35]; and judicious combinations of these approaches. However, despite considerable efforts over the last decade, the direct synthesis of hydrogen peroxide remains a challenging reaction because the hydrogen peroxide yield under intrinsically safe and non-corrosive conditions is still unsatisfactory and the use of caustic additives and H_2/O_2 mixtures causes corrosion and safety issues [36,37].

Herein, we propose an efficient catalyst design based on a selective adsorption deposition method to achieve high reaction performance in the direct synthesis of hydrogen peroxide. The formation of extremely small and monodispersed Pd nanoparticles on an activated carbon support was realized by the combination of the selective adsorption of metal precursor cations on the negatively charged activated carbon surface and the homogeneous surface deposition of palladium hydroxide by hydroxide ions that are slowly generated upon urea decomposition. As will be discussed, the as-prepared Pd/C catalyst showed superior reaction performance compared to the Pd/C catalysts prepared by conventional method. The exceptional catalytic activity is comparable to that of previously reported Pd catalysts supported on various carbon materials.

Moreover, by performing systematic characterizations and test reactions, we elucidated the crucial role of the oxygen groups (particularly the carboxyl groups) of the activated carbon surface in the catalytic performance. Most related studies focused on the changes in the catalytic activity with respect to the different physicochemical properties of various carbon materials [27,38,39]. We believe that the systemically designed selective adsorption deposition method can be extended to other catalyst designs that require highly dispersed active metal sites.

2. Experimental

2.1. Chemicals

Catalyst carrier grade activated carbon (Norit, surface area 1007 m^2/g, pore volume 0.87 cm^3/g, pore diameter 3.47 nm) was received from Carbot. Palladium chloride (99.9%) and tetraamminepalladium(II) nitrate solution (5.0 wt% as Pd) were supplied by Strem-Chemicals. Cerium(IV) sulfate standard solution (0.25 N in 2–3 N sulfuric acid), ferroin indicator (0.1 wt% solution in water), sodium bromide (>99%), 1-decene (>97%), and heptane (99%) were purchased from Sigma-Aldrich. Hydrogen peroxide (34.5%), acetic acid (99.5%), nitric acid (60 wt%), hydrochloric acid (35–37%), sulfuric acid (96%), urea (99%), sodium hydroxide (98.0%), sodium carbonate anhydrous (99.5%), sodium bicarbonate (99%), and methanol (99.5%) were supplied by Samchun Chemicals in Korea. All the chemicals were used as-received without further purification.

2.2. Surface modification of the activated carbon support

For the introduction of oxygen-containing functional groups on the surface, activated carbon was refluxed for 6 h in acid or acid/oxidant solutions of different concentrations: 1 wt% HNO_3, 10 wt % HNO_3, and 10 wt% HNO_3/10 wt% H_2O_2. After the surface modification, the resulting activated carbon was thoroughly washed with water and dried in an oven at 383 K for 12 h. The samples were stored in a desiccator under nitrogen before use.

2.3. Preparation of the Pd/C catalysts using anionic and cationic metal precursors

The Pd/C catalyst was prepared via a well-known deposition-precipitation method with the anionic palladium precursor H_2PdCl_4 [40–43]. Activated carbon (1 g) suspended in deionized water was mixed with a solution of the anionic metal precursor ($PdCl_2$ dissolved in 0.2 M HCl), and the mixed solution was stirred at 298 K for 2 h (Pd intake 5 wt%). After heating to 353 K, 0.5 M NaOH solution was added to the suspension until the pH of the mixed solution reached 12. After additional stirring for 2 h, a reduction reaction was performed by bubbling hydrogen (20 mL/min) at the same temperature for 2 h under vigorous stirring. During these steps, the temperature of the suspension was maintained at 353 K using a double-jacked reactor connected to a circulator. At the end of the reduction, the catalyst was filtered at room temperature, thoroughly washed with deionized water, and dried overnight at 393 K.

The preparation of a Pd/C catalyst using the cationic palladium precursor $Pd(NH_3)_4(NO_3)_2$ was carried out by a modified selective adsorption deposition method [44,45]. Activated carbon was suspended in deionized water, and the suspension was adjusted to pH 4 by the addition of HNO_3. After adding the tetraamminepalladium(II) nitrate solution at 298 K, the mixed solution was stirred for 2 h to allow the selective adsorption (Pd intake 5 wt%). After the temperature was raised to 353 K, urea was added under vigorous stirring. The pH of the resulting mixture gradually increased and finally reached a constant value after 12–24 h; therefore, the deposition procedure was continued for 24 h. The pH of the suspension was monitored during this step, and the amount of urea was adjusted to maintain the final pH at ca. 6.3. After the deposition, the slurry was filtered, thoroughly washed with deionized water, and dried overnight at 393 K. The sample was reduced in the presence of mixed N_2/H_2 gas (50 mol% H_2, 100 mL/min) at 473 K for 3 h (heating rate = 5 K/min).

2.4. Characterization of the surface-modified activated carbon and catalyst

The textural properties of the surface-modified activated carbons, such as the specific surface area, pore volume, and pore diameter, were determined by N_2 adsorption using a BELSORP-Max (BEL, Japan) at 77 K. Prior to adsorption, the samples were degassed at 423 K overnight under vacuum. The distribution of the oxygen-containing functional groups on the activated carbon surface was determined by titration following Boehm's method [46]. The temperature-dependent evolution of the decomposition gases from an activated carbon domain was monitored by temperature-programmed desorption-mass spectrometry (TPD-Mass, BEL-CAT-Mass, Japan). Before the experiment, the samples were dried using helium flowing at the rate of 100 mL/min at 373 K for 2 h. The temperature of the samples was increased to 1273 K at a ramping rate of 5 K/min, and the decomposition gases were detected using a mass spectrometer. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) of the surface-modified activated carbon were recorded using a FT-IR spectrometer (Nicolet iS50 with DTGS detector, Thermo Fischer Scientific, USA) equipped with a diffuse IR chamber (Pike Technology, USA). UV–visible spectra were collected using a Hitachi U-2900 UV–Vis spectrophotometer. Zeta potential measurements were carried out in a wide pH range 2–12 using a zeta potential analyzer (ELS-8000, Otsuka Electronics, Japan). The Pd content loaded on the activated carbon was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer OPTIMA 7300 DV. For ICP analysis, palladium was extracted using HNO_3/HCl mixture solution under microwave digestion. The Pd content on an activated carbon support was measured three times and the average value was used. The oxygen/carbon atomic ratio of the surface-modified activated carbon and the binding energies of Pd in the Pd/C catalysts were determined by X-ray photoelectron spectroscopy (MultiLab 2000, Thermo VG Scientific, UK)