Direct synthesis of hydrogen peroxide from hydrogen and oxygen over single-crystal cubic palladium on silica catalysts

Seongmin Kim[a], Dae-Won Lee[a,**], Kwan-Young Lee[a,b,*]

[a] Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seoul 136-713, Republic of Korea
[b] Green School, Korea University, 145 Anam-ro, Seoul 136-713, Republic of Korea

ARTICLE INFO

ABSTRACT

The activities of Pd metal catalysts for direct hydrogen peroxide synthesis are influenced by the morphological and crystallographic properties of the Pd species. We prepared {1 0 0}-facet-enclosed Pd nanocubes of uniform shape, size, and crystallinity using an aqueous colloidal method. The nanocube size was adjusted, without affecting the shape, by changing the composition of the halide-ion capping agent. The Pd nanocubes were impregnated on silica, and tested as a catalyst in direct hydrogen peroxide synthesis. The {1 0 0} Pd facet catalyzed hydrogen peroxide formation but promoted side reactions, decreasing hydrogen peroxide selectivity; the selectivity was improved by blocking active sites on the {1 0 0} facet with bromide ions.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Face-centered cubic (fcc) noble metal nanoparticles (Pd, Au, Pt, etc.) of specific shapes and sizes can be synthesized using colloidal methods, in which metal precursors are dispersed over a homogeneous surfactant solution and precipitated to metallic crystallites with control of the nucleation and growth rates [1–4]. There are many papers in the literatures on the roles of synthetic reagents such as reducing agents, stabilizers (including surfactants), capping agents, and etchants in determining the sizes and/or shapes of nanoparticles [1–7]. The shape of an fcc nanoparticle determines the facet exposed on its surface: cubic, octahedral, and decahedral nanoparticles are enclosed by {1 0 0}, {1 1 1}, and {1 1 0} facets, respectively [1,8]. Truncated cubic and truncated octahedral nanoparticles are enclosed by {1 1 1}/{1 0 0} facets in different ratios [9]. In general, the formation of multi-facet-enclosed nanoparticles is thermodynamically favored compared with single-facet-enclosed nanoparticles. To promote the formation of nanoparticles enclosed by a single facet, it is necessary to use a specific capping agent in the synthesis. It is known that bromide ions and citric acid preferentially promote the formation of {1 0 0}

and {1 1 1} facets, respectively [1]. The facet determines the way in which metal atoms are arranged on a surface, so the nanoparticles enclosed by a specific facet (i.e., nanoparticles of a specific shape) exhibit unique catalytic properties and activities. For example, cubic Pd nanoparticles are more active than octahedral Pd nanoparticles in electrocatalytic oxygen–reduction reactions [10]. In the hydrogenation of benzene with Pt catalysts, the selectivities for cyclohexane and cyclohexene depend on the shape of the Pt particles [11]. Cyclohexane and cyclohexene are both produced on cuboctahedal Pt nanoparticles, but only cyclohexane is produced on cubic nanoparticles; these selectivities are the same as those exhibited by Pt {1 1 1} and Pt {1 0 0} model surface.

It is therefore highly anticipated to use shape-controlling techniques in the design of noble metal catalysts, especially those for structure-sensitive reactions of high industrial value. In this work, we studied the use of cubic Pd nanoparticles (i.e., Pd nanocubes) in the direct synthesis of hydrogen peroxide by oxidation of hydrogen with molecular oxygen. This reaction is an environmentally benign and economically attractive alternative to the commercial process used for producing hydrogen peroxide (Riedl–Pfleiderer or anthraquinone process). It is usually progressed in a three phase (gas–liquid–solid) reactor where the gases (hydrogen and oxygen) are fed to the aqueous slurry of catalyst. The hydrogen peroxide is formed on the solid catalyst and accumulated in the aqueous phase in which acid (phosphoric or sulfuric acid) is dissolved to protect hydrogen peroxide from dissociation. On the catalyst, the hydrogen peroxide formation (Route I in Fig. 1) competes with several side

---

* Corresponding author. Tel.: +82 2 3290 3299; fax: +82 2 926 6102.
** Corresponding author. Tel.: +82 2 3290 3727; fax: +82 2 926 6102.
E-mail addresses: stayheavy@korea.ac.kr (D.-W. Lee), kylee@korea.ac.kr (K.-Y. Lee).
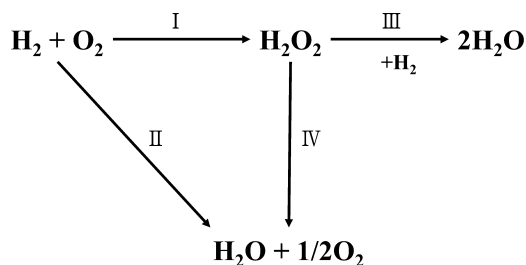
$$H_2 + O_2 \xrightarrow{\text{I}} H_2O_2 \xrightarrow[+H_2]{\text{III}} 2H_2O$$

(with routes II and IV leading to)

$$H_2O + 1/2O_2$$

Fig. 1. Reactions involved in the direct synthesis of hydrogen peroxide.

reactions, that is, the combustion of hydrogen (Route II in Fig. 1) and dissociation and hydrogenation of hydrogen peroxide (Route III and IV in Fig. 1). Hence, the selectivity of hydrogen peroxide is an important index along with H_2 conversion for evaluating catalytic activities in direct hydrogen peroxide synthesis.

Palladium-based catalysts are the most widely used and studied catalysts for this reaction [12–22]. The morphological and crystallographic properties of the Pd metal species are one of the critical factors governing the catalytic activity. Menegazzo et al. reported that a less energetic (or less defective) Pd surface, which adsorbs oxygen without dissociation, is necessary for hydrogen peroxide production [13]. Edwards et al. studied Pd–Au alloy catalysts and suggested that addition of a small amount of Au changed the physical or electronic structure of Pd in a way that increased hydrogen peroxide selectivity [14]. Zhou et al. claimed that the {1 1 0} facet of Pd has a desirable atomic configuration for hydrogen peroxide production, whereas the {1 0 0} and {1 1 1} facets promote water-producing side reactions, suppressing the selectivity of hydrogen peroxide [15]. However, there are different opinions as to which is the most desirable Pd facet for the synthesis of hydrogen peroxide. Rossi et al. asserted that the {1 0 0} Pd surface is more active than the polycrystalline surface for hydrogen peroxide production [16]. According to the density functional theory study by the {1 1 1} facet is the most suitable among the low-index facets of Pd, such as {1 0 0}, {1 1 1}, and {1 1 0}, for the production of hydrogen peroxide [17]. In most of these studies, the catalysts contained the palladium species which were polycrystalline or alloy, so the results gave no information on how the morphological properties of the single-shape Pd crystals are related to its catalytic activity. Some studies used a Pd disk aligned with a single-crystal facet [16], and these gave valuable information regarding the intrinsic activity of a specific Pd facet, but inevitably ignored the influence of the properties of impregnated Pd metal, such as the particle size and interactions with the support material. Therefore, a systematic study of Pd catalysis investigating the catalytic activities of single-shape Pd nanocrystals, each of which is enclosed by its own crystallographic facet is needed [1]. Such information would be helpful in designing Pd-based catalysts for various applications, including hydrogen peroxide synthesis.

In this study, we synthesized single-crystal Pd nanocubes enclosed by {1 0 0} facets, in an aqueous phase, using L-ascorbic acid as a reductant (to reduce metal cations to metal), polyvinylpyrrolidone (PVP) as a stabilizer (to prevent nanoparticle agglomeration), and halide ions (Br^- or $Br^- + Cl^-$) as a capping agent (to stabilize a specific facet on the Pd particle surface) [1,7]. The Pd nanocubes were impregnated on a silica support, and the catalytic activity of the silica-supported Pd nanocubes in the direct hydrogen peroxide synthesis was evaluated. In many cases, halide ions are added to the reaction to improve the selectivity of hydrogen peroxide [18,19]. The halide ions are adsorbed on the Pd surface and influence the electronic state of Pd, which leads to the suppression of side reactions, promoting the selectivity of hydrogen peroxide. The way in which halide ions influence the selectivity of

hydrogen peroxide is probably characteristic of a specific Pd facet. We therefore examined the influence of halide ions on the catalytic activity of {1 0 0}-facet-enclosed Pd nanocubes for hydrogen peroxide production.

2. Experimental

2.1. Synthesis of Pd nanocubes

The Pd nanoparticle synthesis was based on the work of Lim et al. [1]. An aqueous solution (16 mL) containing L-ascorbic acid (0.680 mmol; Sigma–Aldrich), PVP (0.189 mmol; molecular weight 55,000 g/mol; Sigma–Aldrich), and a halide-ion capping agent (10 mmol of KBr, 5 mmol of KBr, or a mixture of 0.1 mmol of KBr and 4.9 mmol of KCl) was prepared. The solution was preheated at 80 °C for 5 min, and then Na_2PdCl_4 aqueous solution (63.8 mM, 6 mL) was added to the solution. Precipitates began to form and stirring was continued for 3 h. The slurry was mixed with acetone in a volume ratio of 1:10 and the Pd nanoparticles were collected by centrifuging the slurry at 3500 rpm for 10 min. The collected nanoparticles were washed several times with deionized (DI) water.

2.2. Immobilization of Pd nanocubes on silica

The collected Pd nanoparticles were dispersed in deionized water (4 mL). The Pd slurry was impregnated on amorphous silica gel (4 g, specific surface area = 291 m^2/g, pore volume = 1.105 cm^3/g; Sigma–Aldrich) and the vacuum dried at 60 °C overnight.

2.3. Characterization

For transmission electron microscopy (TEM), the sample was dispersed in ethanol, and dropped on a Cu grid and dried under ambient air conditions. TEM images were obtained using a field-emission TEM microscope (Tecnai G^2 F30 ST, FEI), operated at 300 kV. The average size, aspect ratio, and production yield of the nanocubes were determined by measuring 120 particles in the TEM image. X-ray diffraction (XRD) patterns were obtained using a D/MAX-2500/PC diffractometer (Rigaku), operated at 40 kV and 200 mA with Cu Kα1 radiation (λ = 1.5406 Å). The loading amount of Pd on the silica was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; iCPA-6300 Duo, Thermo Scientific).

2.4. Catalytic activity tests: direct synthesis of hydrogen peroxide

The catalytic activity tests were performed using the reaction conditions described in our previous paper [20]. The reactions were carried out at 20 °C and atmospheric pressure for 3 h. The catalyst loading was 0.2 g. The reaction medium was 150 mL of an ethanol (20%)–DI water solution (0.03 M) of phosphoric acid, with or without 0.9 mM KBr. The total gas flow rate was 22 mL/min, and the hydrogen/oxygen ratio was 1/10. The hydrogen peroxide concentration was measured using iodometric titration. The concentration of hydrogen was measured using a gas chromatograph (Younglin, ACME6000) equipped with a thermal conductivity detector and a Carbosieve S^{II}-packed column.

3. Results and discussion

TEM images of the synthesized Pd nanoparticles are shown in Fig. 2(a)–(c); the halide-ion capping agent contents were 10 mmol of KBr, 5 mmol of KBr, and 0.1 mmol of KBr + 4.9 mmol of KCl,