Role of Pt atoms on Pd(1 1 1) surface in the direct synthesis of hydrogen peroxide: Nano-catalytic experiments and DFT calculations

Suyeon Quon [a],[1], Deok Yeon Jo [a],[1], Geun-Ho Han [a], Sang Soo Han [b], Myung-gi Seo [a],*, Kwan-Young Lee [a],**

[a] Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seoul 02841, Republic of Korea
[b] Computational Science Research Center, Korea Institute of Science and Technology (KIST), Hwarangno 14-gil 5, Seoul 02792, Republic of Korea

A B S T R A C T

Pd-Pt bimetallic catalysts have been studied for improvement of H_2O_2 selectivity in direct synthesis of H_2O_2; however, the role of Pt on the Pd surface has not been clearly identified. Herein, we investigated the role of Pt atoms on Pd(1 1 1) facets by realizing the surface in two different ways: nano-synthesis and density functional theory (DFT) calculation model. Pd(1 1 1) were modified into 3 kinds of Pd-Pt-alloyed surfaces, a minor Pt-substituted Pd, a major Pt-substituted Pd and a Pt-shell, covering bulk Pd. We successfully embedded Pt atoms in the octahedral Pd surface. Reaction tests showed that the minor Pt-substituted octahedral Pd catalyst had the highest H_2O_2 selectivity, production rate and the lowest H_2O_2 decomposition rate. The experimental results were consistent with our DFT calculations which predicted the lowest activation barrier for the O_2 hydrogenation step and the highest one for the H_2O_2 dissociation step on the minor Pt-substituted Pd surface.

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1. Introduction

A newly modified Pd catalyst with high hydrogen peroxide selectivity for the direct synthesis of hydrogen peroxide (DSHP) needs to be designed for the commercialization of the DSHP process. Hydrogen peroxide (H_2O_2) is a green and versatile oxidant in industrial applications such as pulp and paper bleaching, sterilant, chemical syntheses and wastewater treatment [1–11]. DSHP with Pd-modified catalysts has been proposed to replace a conventional process because of the environmental and economic advantages over time [3,5–10,12–19]. DSHP is eco-friendly because it does not require any hazardous compounds and produces only water as a byproduct [5], and is economical for the immediate supply of hydrogen peroxide to the subsequent on-site processes, *e.g.*, direct synthesis of hydrogen peroxide – hydrogen peroxide propylene oxide (DSHP-HPPO) [9,10,20–22]. DSHP-HPPO has been proposed as an integrated process, where an initial DSHP process produces hydrogen peroxide that is immediately supplied to an HPPO process that oxidizes propylene into propylene oxide

[20,21]. However, DSHP has too low selectivity to be commercialized because of spontaneous side reactions, such as water formation (see Scheme 1) [5,8,23,24]. Thus, it is necessary to develop a newly modified Pd catalyst with high H_2O_2 selectivity.

In DSHP, nondissociative adsorption of O_2 and production of OOH^* species (O_2 hydrogenation) on the catalytic surface are known to be the key reaction steps for improved DSHP selectivity [12,25], which is not directly explained from common catalytic characterizations. Thus, density functional theory (DFT) calculations and morphology-controlled nanocatalytic experiments can be more powerful tools than any other general characterizations to investigate the behaviors of reactants on a controlled surface, especially when studying DSHP. DFT calculations provide independent information obtained from only one variable, such as facet or metal composition, while tangible catalysis gives combined results from many variables. Morphology-controlled nanocatalytic experiments provide DFT calculations relevant information to guide the numerous calculated results to be interpreted in the right direction. Previous research reported that Pd(1 1 1) facets were more advantageous in H_2O_2 selectivity than Pd(1 0 0) facets [26], which has already been proved experimentally by a previous research that Pd nanooctahedra enclosed by (1 1 1) facets showed much higher selectivity than Pd nanocubes enclosed by (1 0 0) facets [27]. Pd-based bimetallic catalysts (*e.g.*, Au, Pt, Sn, and Te) have recently been introduced as a successful way to improve H_2O_2 selectivity [28–30]. Especially, it has been reported that a minor

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* Corresponding author at: Lotte Chemical, 115 Gajeongbuk-ro, Daejeon, 34110, Republic of Korea.
** Corresponding author.
E-mail addresses: bluebird18@korea.ac.kr (M.-g. Seo), kylee@korea.ac.kr (K.-Y. Lee).
[1] These authors contributed equally to this work.