Designed Pd nanoparticles for direct synthesis of hydrogen peroxide

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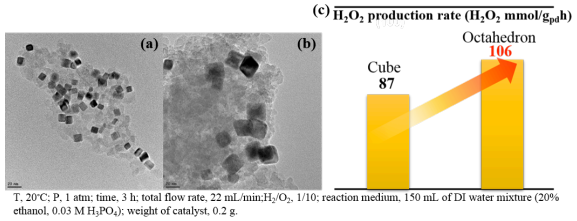
Hydrogen peroxide (H_2O_2) has been used in various chemical industries such as bleaching agent of pulp, paper and raw material for producing chemicals *etc*. H_2O_2 can be synthesized by direct synthesis process from H_2 and O_2, and the palladium (Pd) is widely used active metal. In reaction mechanism of direct H_2O_2 synthesis, decomposition of O_2 and H_2O_2 should be inhibited to increase H_2O_2 selectivity.

Density functional theory (DFT) study has allowed deeper understanding of palladium's excellent activity in correlation with the physical structure and electronic state and serve as a guide for optimized design of the catalyst. Therefore, optimal catalysts of direct H_2O_2 synthesis could be synthesized as a combined result of DFT predictions and experiments.

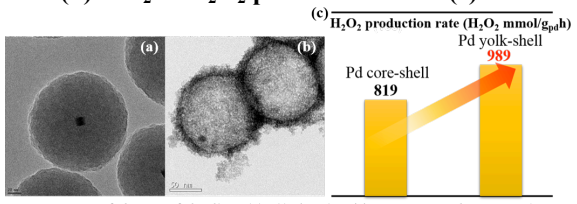
According to the DFT results, {100} facet-enclosed cubic Pd has lower O_2 decomposition energy barrier than {111} facet-enclosed octahedral Pd [1]. Cube- and octahedron-shaped Pd catalysts were synthesized and applied in direct synthesis of H_2O_2, and Pd octahedral catalyst yielded higher H_2O_2 productivity than Pd cubic catalyst [2]. In addition, size-controlled Pd octahedral catalysts were synthesized to reduce the energetic O_2 dissociative corner & edge sites and to increase less energetic terrace sites. The largest 18-nm-sized catalysts among the tested Pd octahedral nanoparticles of varying sizes showed the highest productivity owing to the highest proportion of the terrace sites [3]. In addition, bimetallic catalysts are being investigated to further increase the activity. Galvanic-replaced Pt-doped Pd octahedral catalysts were examined on H_2O_2 direct synthesis to determine synergistic effect. Also, cubic Pd core-Au shell catalysts were synthesized to study strain effects.

However, the shape- and size-controlled Pd nanoparticles (NPs) were physically detached (55-77%) from support after reaction [2]. Core- and yolk-shell structures were examined as an alternative to prevent the loss of Pd particles. Both structures significantly reduced the loss of NPs (below 5%) during the reaction. Especially, the catalytic activity of yolk-shell structured Pd catalyst was superior because of higher exposed Pd surface area [4]. The micropore channels of the shell, however, limited diffusion of reactant gas molecules and compromised productivity. Therefore, grafted Pd nanoparticles on mesoporous SiO_2 shell (SiO_2@Pd@m-SiO_2) were synthesized to enhance mass diffusion through the pores. Consequently, SiO_2@Pd@m-SiO_2 showed the highest productivity (1090 mmol/g_{Pd}h) among applied catalysts for direct H_2O_2 synthesis [5].



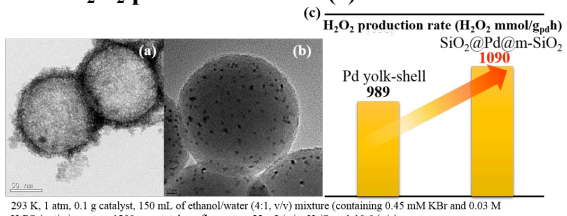
T, 20°C; P, 1 atm; time, 3 h; total flow rate, 22 mL/min;H_2/O_2, 1/10; reaction medium, 150 mL of DI water mixture (20% ethanol, 0.03 M H_3PO_4); weight of catalyst, 0.2 g.

Fig. 1 TEM images of Pd cube (a), octahedron (b)/SiO_2 & H_2O_2 production rates (c)



293 K, 1 atm, 1 mg of Pd, 150 mL of ethanol/water (4/1, v/v) mixture(containing 0.15 mM KBr and 0.03 M H_3PO_4), stirring rate = 1200 rpm, total gas flowrate = 22 mL/min, H_2/O_2= 1/10 (v /v).

Fig. 2 TEM images of Pd core (a), yolk-shell (b) & H_2O_2 production rates (c)



293 K, 1 atm, 0.1 g catalyst, 150 mL of ethanol/water (4:1, v/v) mixture (containing 0.45 mM KBr and 0.03 M H_3PO_4), stirring rate = 1200 rpm, total gas flow rate = 22 mL/min, H_2/O_2 = 1:10 6 (v/v)

Fig. 3 TEM images of Pd yolk-shell (a), SiO_2@Pd@m-SiO_2 (b) & H_2O_2 production rates (c)

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