**The origin of the palladium particle size effects in the direct synthesis
of H₂O₂: Is smaller better?**

Pengfei Tian ^{a,1}, Like Ouyang ^{a,1}, Xingyan Xu ^a, Can Ao ^a, Xinchao Xu ^a, Rui Si ^b,
Xiangjian Shen ^c, Ming Lin ^d, Jing Xu ^{a,*}, and Yi-Fan Han ^{a,c,*}

Affiliations:

^aState Key Laboratory of Chemical Engineering, East China University of Science
and Technology, Shanghai 200237, China.

^bShanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics,
Chinese Academy of Sciences, Shanghai 201204, China.

^cResearch Center of Heterogeneous Catalysis and Engineering Sciences, School of
Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, China.

^dInstitute of Materials Research and Engineering (IMRE), A* STAR, 138634,
Singapore.

*Correspondence to:

E-mail: yifanhan@ecust.edu.cn; xujing@ecust.edu.cn.

Tel: +86-21-64251928. Fax: +86-21-64251928

ABSTRACT:

A series of size-controlled Pd/hydroxyapatite (HAp) catalysts ranging from single sites (Pd clusters) to nanoparticles (d_{Pd} : ~30 nm) was prepared and examined for the H_2O_2 synthesis directly from H_2 and O_2 . A Pd/HAp (d_{Pd} : ~1.4 nm) showed a high selectivity of 94% toward H_2O_2 under mild conditions (283 K and atmospheric pressure). The crystal phase, morphology, surface electronic states and coordination number of Pd particles from atomic level to nano scale were characterized in detail using multi-techniques such as X-rays diffraction, scanning transmission electron microscopy and the extended X-rays absorption fine structure. Density functional theory calculations indicated that Pd clusters in subnano size have the most effective active sites for the selective activation of oxygen hydrogenation, thus resulting in the high catalytic efficiency for H_2O_2 synthesis. This work elucidates those smaller Pd particles only in a proper size-range show the best catalytic performance for H_2O_2 synthesis.

Keywords: size effects, subnano clusters, Pd/HAp catalysts, H_2O_2 synthesis, structure-performance relationship

1. Introduction

The origin of size effects has long been a spotlight in the field of heterogeneous catalysis [1-6]. Nowadays, many efforts have been contributed to the characterization of active sites over catalysts, in which the size of metal particles is usually larger than ca. 2.5 nm, a so-called magic size from non-metallic to metallic property for metal particles [7, 8]. More recent studies have proven that active sites of practical metal catalysts may contain a certain amount of single sites [9-11] or clusters [12], or to say, the metal particles in the subnano size, which probably act as active components [13]. Nevertheless, it is still a great challenge to understand the origin of particle size effects, especially, to establish the structure-performance relationship of those catalysts with subnano size. On the other hand, is the smaller size better for catalysis? This question has intrigued a lot of debate on both academe and industry for the last years, and it is of importance to the rational design and controllable synthesis of industrial catalysts [14-17].

In this work, our strategy is to prepare a series of size-controlled Pd catalysts, which ranges from single sites (atomic level) to nanoparticles (ca. 30 nm). We examine their catalytic performance for the direct H_2O_2 synthesis, which is regarded as a dreamful route to produce this greener oxidant, instead of an alternative of the current Riedl–Pfleiderer process involving sequential hydrogenation and oxidation of an anthraquinone [18]. It will greatly optimize the oxidation processes if coupling with oxidation process using H_2O_2 as an oxidant [19-24]. Actually, high selectivity toward H_2O_2 is difficult to achieve, since most of catalysts that are effective for the

formation of H₂O₂ increase the production of undesirable water as well [25-30]. It is worthy to emphasize that the selective hydrogenation of O₂ is also of great importance to the development of fuel cells [31, 32].

Our preliminary studies have revealed that the electronic structure of the surface Pd atoms in a Pd/TiO₂ catalyst could be tuned by forming Pd–PdO ensembles, and the maximum H₂O₂ selectivity of ca. 60% was achieved without promoters [33]. With the optimization of reaction conditions, such as pressure, solvent, and the addition of promoters and acids, the selectivity could be improved to about 80% [26]. Remarkable increase in H₂O₂ selectivity could be obtained over Pd-M (M: Au, Pt etc.) bimetallic catalysts [34-38]. More recently, the Hutchings' group has reported selectivities of over 95% using Pd-Au and Pd-Sn alloy catalysts [39, 40]. Nevertheless, the achievement of such a high selectivity for monometallic Pd catalysts is still a challenge.

Herein, we prepared a series of Pd (0.5~5.0wt%)/Hydroxyapatite (HAp) catalysts using the ion-exchange method (I.E.) to prepare the single sites catalyst and the incipient wetness impregnation method to control the size of Pd particles. The catalytic performance was examined under mild conditions using a semi-batch micro tri-phase reactor [33]. The microstructure and dimensional constraints of Pd particles and the proximity between metal atoms and clusters are characterized using multi-techniques; meanwhile, the surface structure of Pd particles, especially, the formation of Pd/PdO_x interface and its relevance to the Pd particle size are identified. Finally, the models of active sites are proposed on the basis of density functional

theory (DFT) calculations. We believe the combination of experimental evidences with the DFT calculations can shed a light on the origin of particle size effects on the catalytic performance.

2. Experimental

2.1. Catalyst preparation

HAp, as the support, was prepared by chemical precipitation of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$, more details of the preparation was given in Supplementary Information (SI). The crystal structure of HAp is shown in Fig. S1 [41]. Catalysts were prepared by incipient wetness impregnation using an aqueous solution of PdCl_4^{2-} as described in a previous study [33]. The single-site Pd catalyst was prepared by the ion-exchange method (denoted as Pd(I.E.), in which the HAp (995 mg) was added into 300 mL deionized water and mixed with 1 mL Pd^{2+} solution (0.05 mol/L) for 48 h at 343 K, then filtered and dried at 383 K for another 24 h, the Pd loading is 0.5 wt %.

To investigate the effect of calcination temperature, precursors were firstly pretreated in O_2 (20 mL/min) for 30 min at 473 K, 573 K, 673 K, 773 K, and 873 K, respectively, and then reduced in H_2 (20 mL/min) for another 30 min. The reduction temperature was 473 K for the precursor pretreated in O_2 at 473 K and 573 K for others. The catalysts pretreated in O_2 at 673 K showed the best performance for H_2O_2 synthesis and only ca. 2% leaching of the Pd loading after 5 hour reaction (Table S1). Therefore, prior to the reaction, the precursors of all the catalysts were pretreated in O_2 (20 mL/min) at 673 K for 30 min and then reduced in H_2 (20 mL/min) at 573 K for another 30 min.

2.2. Catalytic reaction

All reactions were carried out under ambient conditions using a modified micro triphase semi-batch reactor. The reagent gases were introduced into the reactor via a premixer and a fine glass frit in sequence, and the slurry containing the catalyst was magnetically stirred to minimize diffusion limitations. The reactor was connected to a gas chromatograph so that the conversion of H₂ could be determined on the basis of a standard curve indicating the quantitative relationship between the conversion of H₂ and the H₂/N₂ area ratio. The conversion of O₂ was also measured with an O₂ balance of over 99%. The concentration of H₂O₂ was analyzed calorimetrically using a UV–Vis spectrophotometer (Epp 2000, Stellar Net Inc.) after complexation with a TiOSO₄/H₂SO₄ reagent.

H₂O₂ selectivity, S_{H₂O₂}, was calculated by Eq.(1):

$$S_{H_2O_2} = \frac{r_{H_2O_2}(\text{mol/h})}{r_{H_2}(\text{mol/h})} \times 100\% = \frac{r_{H_2O_2}(\text{mol/h})}{X_{H_2}Q(\text{mol/h})} \times 100\% \quad (1)$$

where r_{H₂O₂} is the mean rate of H₂O₂ formation calculated based on mol.s vs. time curves as in Fig. 1; r_{H₂} is the mean rate of H₂ consumption calculated based on H₂ conversion (X_{H₂}) and H₂ flow rate (Q, 0.024 mol/h).

The reaction rate for H₂O₂ formation expressed in the turnover frequency (TOF, h⁻¹) was obtained by Eq.(2):

$$r_{H_2O_2, TOF} = \frac{r_{H_2O_2, n_{Pd}}}{D_{particle}} = \frac{r_{H_2O_2} / n_{Pd}}{D_{particle}} \quad (2)$$

where r_{H₂O₂, n_{Pd}} is the mean rate of H₂O₂ formation (r_{H₂O₂}, mol/h) per unit amount of Pd calculated based on the total amount of Pd (n_{Pd}, mol), and D_{particle} is the dispersion of

metal atoms (Eq.(3)) exposure to reactants evaluated on the basis of a hemispheric model:

$$D = 6 \frac{v_m / a_m}{d_{VA}} \quad (3)$$

where v_m ($1.47 \times 10^{-23} \text{ cm}^3$) is the volume occupied by a Pd atom in the bulk of Pd metal, which is given by $v_m = M/(\rho N_A)$, where M (106.42 g/mol) is the atomic mass of Pd, ρ (12.02 g/cm^3) is the mass density and N_A ($6.022 \times 10^{23} \text{ mol}^{-1}$) is Avogadro's number; a_m ($7.93 \times 10^{-16} \text{ cm}^2$) is the surface area occupied by a Pd atom on a polycrystalline surface, given by $a_m = 1/n_s$, where n_s is the number of atoms per unit area in the crystalline planes; and d_{VA} is the volume-area mean diameter or mean particle size obtained from TEM.

In the reaction, an $\text{O}_2:\text{H}_2:\text{N}_2 = 36:9:15$ gas mixture with a flowrate of 60 mL/min was introduced into the reaction system at 283.15 K without special statement. The liquid phase was composed of 60 mL of ethanol that had been acidified with 0.38 mL of concentrated H_2SO_4 . Following each experiment, residual Pd that had been deposited on the frit was removed by ultrasonic cleaning with acidic solution and ultrapure water. In most cases, a yellow–orange solution, resulting from Pd^{2+} , was observed.

Since the gas mixture is still in the explosive regime, care must be taken to avoid contact of the gas mixture with a dry catalyst. This was achieved first by mixing 50 mg of the catalyst with 10 mL of the solution; and then, the slurry was added back into the solution that remained in the reactor. It should be noted that with ethanol as the liquid phase the catalyst remained wet, even in the upper regions of the reactor. 50

mg of catalysts was used for all tests. Further information about experiments has been given in SI.

2.3. Characterizations

A series of characterization methods were used to determine the structure of Pd/HAp catalysts. Ahead of measurements, catalysts were pretreated following the same method used in reactions. All precursors were pretreated in O₂ (20 mL/min) at 673 K for 30 min and then reduced in H₂ (20 mL/min) at 573 K for another 30 min. All samples were protected to avoid the exposure to air before measurements.

Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM 2010F electron microscope operating at 200 kV. The catalysts were first ultrasonically suspended in ethanol, and then one drop of this slurry was deposited on a carbon-coated copper grid. The liquid phase was evaporated before the grid was loaded into the microscope. The size distribution of Pd particles was estimated on the basis of 300 particles.

The Aberration-corrected scanning transmission electron microscopy (STEM) measurements were performed on a FEI Titan 80-300 electron microscope. The STEM resolution is 0.136 nm with the accelerating voltage of 300 kV, and the energy resolution of Tridem Gatan Electron Energy Loss Spectroscopy (EELS) system is 0.7 eV.

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max 2550 diffractometer, with accelerating voltage 40 kV, and detector current 100 mA. Cu-K radiation was used for continuous scanning with a step-size of 0.02° over a 2θ range

of 10°–80° with a scan speed of 4°/min.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo ESCALAB 250Xi spectrometer, using a monochromatic Al-K radiation source (1486.6 eV, a pass energy of 20.0 eV). The base pressure of the instrument is about 1×10^{-9} Torr. The binding energies (BEs) were calibrated using the C1s peak at 284.8 eV as a reference. The instrument was also calibrated using Au wire (Au4f $_{7/2}$ at 84.0 eV). The background of XP spectra caused by inelastic processes was subtracted by the Shirley method.

The extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra of the Pd K edge were measured at the BL14W1 beamline, Shanghai Synchrotron Radiation Facility (SSRF), with electron beam energy of 3.5 GeV under “top-up” mode (current: 220 mA). The samples were measured at room temperature using a fixed-exit monochromator equipped with two flat Si(311) crystals. Data on the catalysts and reference samples (Pd foil and PdO powder) were collected in the fluorescence mode (32-element HPGe detector) or the transmission mode (Oxford ion chamber). Athena and Artemis softwares were used to extract the data and to fit the curves, respectively [42, 43]. The Fourier-transformed curves were fitted in the real space with $\Delta k = 2\text{--}13 \text{ \AA}^{-1}$ and $\Delta R = 1.1\text{--}3.3 \text{ \AA}$ for Pd (k^2 weighted).

Diffuse reflectance infrared fourier transform spectroscopy of CO adsorption (CO-DRIFTS) on the fresh catalysts was conducted in a reaction cell (modified Harricks Model HV-DR2) in order to allow gas to flow continuously through the

catalyst bed (ca. 0.1 g) during spectra acquisition. The spectra were recorded on a Perkin–Elmer Spectrum 100 FT-IR spectrometer at 283.15 K with a resolution of 4 cm^{-1} . All infrared data were evaluated in Kubelka–Munk units, which are linearly related to the absorber concentration in spectra.

Temperature-programmed desorption (TPD) experiments were performed with a micro fixed-bed reactor connected to a GC-QMS (HPR-20, Hiden Analytical Ltd.), where masses of m/e 2 (H_2), 15(CH_4), 18 (H_2O), 32 (O_2), 40 (Ar), and 44 (CO_2) were monitored.

In order to further detect the residual Cl^- on the catalyst, 0.5 g catalyst powder was treated by microwave digestion, and the solution was tested by an ion chromatograph (ICS-2000, Dionex, USA), which was equipped with an IonPac AG18 + AS18 column. KOH(5 mM) was used as the mobile phase.

2.4 Computational models and methods

DFT calculations were performed using the Vienna ab-initio simulation package (VASP) [44, 45]. A plane-wave basis set with a cut-off energy of 400 eV was used to expand the Kohn–Sham wave functions. The interactions between the ionic cores and valence electrons were described using a projector augmented wave (PAW) method [46, 47], and the exchange-correlation effects were self-consistently described within the Perdew-Burke-Ernzerh of generalized gradient approximation (GGA-PBE) [48, 49]. The occupation of electronic states was determined using Gaussian smearing (the Methfessel-Paxton method [50] for Pd(111) model), and the smearing width was 0.2 eV. Optimized geometries were obtained by minimizing the root mean square (rms)

forces on the atoms until they are smaller than 0.05 eV/Å.

Pd₁/HAp, Pd₃/HAp and Pd₁₀/HAp models were built to simulate the Pd single sites and the Pd clusters supported on the HAp surface, and Pd₃ and Pd₁₀ models were built to simulate the pure Pd clusters for the reference. Pd(111) was adopted to model relatively large Pd particles [32, 36, 51, 52]. For Pd₃ and Pd₁₀ models, a 15×15×15 Å³ cubic supercell was adopted to avoid interactions between adjacent periodic images, and the Brillouin zone was sampled with the Gamma point only. HAp was modeled by a half-layered (100) slab with a (1×2) unit cell. All Pd atoms, reactants, and the topmost fraction layer of HAp were relaxed. The calculated lattice constants for HAp are $a = 9.424 \text{ Å}$ and $c/a = 0.730$. Some possible positions of the Pd clusters with respect to HAp(100) were tested to identify the most stable structure. Pd(111) was modeled as a four-layered slab with a (3×3) unit cell, of which the topmost two layers were relaxed. A vacuum spacing of 12 Å along the normal direction (z) to the surface and a 3×3×1 Monkhorst-Pack *k*-point mesh were used for the Pd clusters on HAp and Pd(111). All transition states were found using the climbing image nudged elastic band (NEB) method [53] and confirmed via vibrational analysis.

The reaction energies (ΔE) of each elementary step were calculated by Eq.(4):

$$\Delta E = E_{FS} - E_{IS} \quad (4)$$

E_{FS} and E_{IS} are the total energies of the final state (FS) and initial state (IS) of the minimum-energy path (MEP), respectively. The activation barriers (E_a) of the elementary steps were calculated by Eq. (5):

$$E_a = E_{TS} - E_{IS} \quad (5)$$

E_{TS} is the energy of the transition state (TS) of MEP. The zero point energy (ZPE)

correction is included into the reaction energy and activation barrier as Eq. (6):

$$ZPE = \sum_i^{\#vibs} \left(\frac{1}{2}\right) h\nu_i \quad (6)$$

where h and ν_i are Planck constant and the calculated vibrational frequencies, respectively.

2.5 Reaction constants and equilibrium constants

Reaction constants and equilibrium constants of the dissociation of O₂ and the formation of OOH were calculated with statistical treatment of results of DFT calculations (Table S2). The rate constant (k) in Eq.(7) is defined in terms of transition state theory (TST) [54]:

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G_a}{k_B T}\right) \quad (7)$$

Where k_B and T represent the Boltzmann factor and reaction temperature, respectively. ΔG_a is the change of the standard molar Gibbs free energy between transition state (TS) and initial state (IS) of elementary steps. The reaction temperature, $T = 283.15$ K, was consistent with that for experiments.

The equilibrium constants (K) were calculated by Eq.(8) [54]:

$$K = \exp\left(\frac{-\Delta G}{k_B T}\right) \quad (8)$$

ΔG is the change of the standard molar Gibbs free energy between the final state (FS) and the initial state (IS) of elementary steps.

The Gibbs free energies of all surface intermediates were calculated by Eq. (9):

$$G(T) = E_{DFT} + ZPE + \int_0^T C_{V,vib} dT - T \cdot S(T) \quad (9)$$

Where E_{DFT} , $C_{V,vib}$, and $S(T)$ are the total energy from DFT calculation, heat capacity,

and entropy, respectively. Only vibration modes were taken into account, since no gaseous molecule was considered to involve the two elementary steps. Therefore, ΔG_a and ΔG can be calculated by Eqs (10-11):

$$\Delta G_a = E_a + (ZPE_{TS} - ZPE_{IS}) + [(\int_0^T C_{V,vib} dT)_{TS} - (\int_0^T C_{V,vib} dT)_{IS}] - T \cdot [S(T)_{TS} - S(T)_{IS}] \quad (10)$$

$$\Delta G = \Delta E + (ZPE_{FS} - ZPE_{IS}) + [(\int_0^T C_{V,vib} dT)_{FS} - (\int_0^T C_{V,vib} dT)_{IS}] - T \cdot [S(T)_{FS} - S(T)_{IS}] \quad (11)$$

The corrections of entropy, $S(T)$, and the heat capacity, $C_{V,vib}$, are evaluated following Eqs. (12-13) [35, 55]:

$$S(T) = k_B \sum_i^{\#vibs} \left[\frac{h\nu_i}{k_B T (e^{\frac{h\nu_i}{k_B T}} - 1)} - \ln(1 - e^{-\frac{h\nu_i}{k_B T}}) \right] \quad (12)$$

$$\int_0^T C_{V,vib} dT = \sum_i^{\#vibs} \frac{h\nu_i}{(e^{\frac{h\nu_i}{k_B T}} - 1)} \quad (13)$$

The dissociation of O_2 is defined as Eq. (14):

The formation of OOH is defined as Eq. (15):

Two descriptors, the ratio of the rate constant of OOH formation to that of O_2 dissociation (R_A , Eq. (16)) and the ratio of equilibrium constant of OOH formation to that of O_2 dissociation (R_B , Eq. (17)), are defined here to evaluate the performance of Pd/HAp catalysts.

$$R_A = \frac{k_{OOH}}{k_{O_2}} \quad (16)$$

$$R_B = \frac{K_{OOH}}{K_{O_2}} \quad (17)$$

Where k_{OOH} and K_{OOH} are rate constant and equilibrium constant of the OOH

formation; k_{O_2} and K_{O_2} are rate constant and equilibrium constant of the O_2 dissociation.

3. Results and discussion

3.1 Catalytic performance

As shown in Fig. 1 and Table 1, no H_2 conversion was measured for the catalyst prepared by Pd(I.E.). A selectivity of 94% and a rate of 284 h^{-1} were determined for 0.5 wt% Pd. Such a high selectivity achieved over a Pd alone catalyst without any promoter, to the best of our knowledge, has been rarely reported so far. With increasing the Pd loading, the rate was increased to 340 h^{-1} , while the selectivity dropped down to 67% over 1.0 wt% Pd, continuously decreased to 197 h^{-1} and 43% over 5.0 wt% Pd. Obviously, both the selectivity and rate of Pd catalysts depend highly on the Pd loading.

Meanwhile, the effect of contact time (due to the change of the Pd loading) on H_2O_2 selectivity had also been ruled out by well-designed experiments (Table S3). Moreover, the potential effect from the leached Pd and residual Cl^- were investigated, of which the influences were hardly detectable on the reaction, as listed in Table S3 and S4.

3.2. Size distribution and morphology of Pd particles

XRD patterns showed that the framework of HAp was rather stable during the preparation process (Fig. 2). In the meantime, almost no diffraction peak of Pd crystalline can be determined for 0.5wt % and 1.0 wt % Pd catalysts, suggesting that the size of Pd particles are no larger than 3.0 nm (a limit for XRD analysis). A small

peak at 40.1° , assigned to the Pd(111) plane, emerged with the increasing of the Pd loading from 2.0 to 5.0 wt %. The same tendency was also revealed by BF-TEM images (Fig. 3). The size of Pd particles was estimated to be ca. 1.6 nm for 0.5 wt % Pd, and increased to ca. 2.6 nm for 5.0 wt % Pd; meanwhile, ca. 1.4 nm for 0.5 wt % Pd was observed using the annular dark-field TEM (ADF-TEM) (Fig. 3F). **Notably, after 2 hour reaction, the average size of 0.5 wt % Pd and 5 wt % Pd catalysts changed to ca. 1.8 nm and 3.1 nm, respectively (Fig. S2). We deduce that catalytic reactions would enhance the mobility of Pd particles on the HAp surface, thus lead to a mild aggregation.** A typical chemical composition for 1.0 wt% Pd was identified by EDS as well (Fig. S3).

Taking a close look at those particles by STEM (Fig. 3H), we did not observe any clear-cut crystal-facet or quasi-crystal Pd phase, while **spherical** Pd particles were randomly stacked on the HAp surface. Smaller Pd particles were further determined using EXAFS, the data was analyzed following the procedure in Figures **S4-S6**. As shown in Fig. 4 and Table 2, **there was no measurable Pd-Pd bond for Pd(I.E.)**, indicating that **mono-dispersed or isolated Pd** atoms were predominant on the surface [56]. For 0.5 wt % Pd, there exists a Pd-O bond of 2.11 ± 0.03 Å and a Pd-Pd bond of 2.80 ± 0.03 Å with a coordination number (CN) of 1.1 ± 0.6 , suggesting that the Pd clusters with 2-3 Pd atoms can be stabilized on HAp. With the combination of EXAFS with TEM results, we assume three types of Pd particles in 0.5 wt % Pd: mono-dispersed Pd atoms (zero-dimension (0D)), subnano Pd clusters with a few Pd atoms (two- or three-dimensions (2D or 3D)) and Pd nanoparticles with crystalline

phase (three-dimension (3D)). The low CN of the Pd-Pd bond hints that mono-dispersed Pd atoms and Pd clusters are the dominant active species for 0.5 wt % Pd, of which the size of Pd particles should be even less than 1.4 nm with considering the detection limit of TEM.

For 1.0 wt % Pd, a Pd-O bond of 2.16 ± 0.03 Å with a CN of 4.8 ± 2.0 was determined. The Pd-Pd bond of 2.74 ± 0.04 Å, close to the Pd-Pd distance in Pd crystals (2.73 Å), has a CN of 6.0 ± 0.8 , driven from larger nanoparticles. The average size of ca. 2.0 nm was evidenced by both EXAFS and TEM. This catalyst is composed of mono-dispersed Pd atoms (0D) and subnano Pd clusters (2D or 3D).

With further increasing the Pd loading (2.0~5.0 wt %), two kinds of Pd-O bonds can be detected. One Pd-O bond of 2.06 ± 0.02 Å is attributed to PdO_x species, while the other Pd-O bond of 2.58 ± 0.04 Å corresponds to weakly adsorbed O₂ species, the Pd-Pd bond remains 2.73 ± 0.01 Å; meanwhile, the CN of the Pd-O bond decreased gradually from 2.2 ± 0.7 to 1.6 ± 0.8 with a rise in the Pd loading. It suggests that the ratio of PdO_x/Pd get smaller with the increasing of Pd loadings, an indicative that more metallic Pd atoms are stable on the catalyst surfaces. TEM images reveal that the average size of Pd particles for these catalysts is calculated to be ca. 2.5 nm.

Both TEM and EXAFS results have evidenced that the size of Pd particles could be effectively manipulated with varying the Pd loading. Importantly, the highest selectivity of 94% was measured for 0.5 wt % Pd (d_{Pd} : ca. 1.4 nm). In order to investigate the size effects on the catalytic performance, we further synthesized two catalysts with average Pd sizes of 22.0 ± 7.8 nm and 31.6 ± 13.2 nm (Fig. S2). It was

found that the selectivity was unaffected with increasing the particle size above 2.5 nm. This issue will be further discussed later.

On the other hand, *in situ* Infrared (IR) spectra (Fig. S7) revealed a decrease in the intensity of the characteristic peak of OH in HAp (3574 cm^{-1}) with the rise of Pd loading. This fact indicates that the cleavage of OH is induced by Pd atoms through forming a Pd-O bond, which is supposed to stabilize Pd particles.

3.3. Electronic structure of Pd particles

The electronic structure of the surface Pd atoms was characterized by *in situ* CO-DRIFT spectra (Fig. 5). The decrease in Pd particle size led to a rise in the linear CO adsorbed on atop sites (2091 cm^{-1}), while the number of CO adsorbed on bridged ($1988\sim1964\text{ cm}^{-1}$) and three-fold ($1913\sim1873\text{ cm}^{-1}$) sites decreased gradually [57, 58]. It is noted that there is no vibrational band for both HAp and Pd(I.E.) catalysts, so that we can safely exclude any signals from support, while the number of isolated Pd atoms is perhaps too small to yield vibrational band for the latter. The linear band at 2091 cm^{-1} detected for 0.5~2.0 wt % Pd catalysts indicates the formation of the highly dispersed metallic Pd atoms and clusters, corresponding to 0D and 2D particles; the band intensity remained unchanged with the rise in the Pd loading, we infer the formation of subnano particles is primarily affected by the local environment on the HAp surface. In the meantime, the several bridged bands appeared for 0.5 wt % Pd and their intensities increased with the Pd loading, which hints the production of tightly compacted Pd clusters or larger Pd particles in 3D. In particular, the growing bands ($1913\sim1873\text{ cm}^{-1}$) assigned to hollow sites indicate more adsorption sites

composed of high density of Pd atoms. Furthermore, the linear band disappeared completely for 3.0 wt % and 5.0 wt % Pd, which might suggest that the subnano Pd particles in 0D and 2D unlikely exist for both catalysts, due to the feasible coalescence of Pd particles during the preparation process.

XPS spectra (Fig. 6) show the different oxidation states of the Pd surface atoms. Only weak signals for the 0.5 wt % Pd catalyst exist because of the low concentration of Pd atoms. The metallic Pd (Pd 3d_{5/2}=335.5eV) was the predominant species for both 5 wt % Pd and 3 wt % Pd; the upshift of the BE of Pd 3d_{5/2} from 335.5 eV (5 wt % Pd, d_{Pd}: ca. 2.6 nm) to 336.5 eV (0.5 wt % Pd, d_{Pd}: ca. 1.4 nm) was measured as well. On the basis of those results, we propose a surface transformation from Pd⁰ to Pd^{δ+} with the decreasing of Pd particle size in the subnano range. The oxidation of surface Pd atoms on supported catalysts has proven to be prone at room temperature with the strong metal support interaction [59]. Herein, we propose that the generation of Pd^{δ+} comes from the reaction between Pd and hydroxyls of HAp.

The formation of PdO_x was further evidenced by O₂-TPD profiles (Fig. 7). Strong peaks in the region of 777-900 K can be assigned to atomic oxygen resulting from the decomposition of PdO_x [60-65], because the desorption temperatures of dioxygen are usually lower than 600 K. It was reported on a Pd/SiO₂ catalyst that bulk PdO_x cannot be formed until 623 K [66], indicating that the influence of exposure to air at room temperature should be trivial. Therefore, the peak of PdO_x may result from the reaction between Pd and the hydroxyls of HAp with the increase in temperature during the TPD test. It suggests that HAp has significant promotional effects on the

oxidation of Pd nanoparticles. The peaks centered at 373 K and 573 K can be contributed by the surface adsorbed oxygen species on Pd particles. The decrease in the Pd loading could reduce the atomic oxygen, but increase adsorbed dioxygen, it is in line with the analysis of EXAFS.

3.4. The structure models of active sites

In order to get deep insights into the size effects on the catalytic performance, we simulated the structure of active sites in Pd particles by DFT calculations. A series of models for active sites (Fig. 8) were proposed: mono-dispersed single Pd sites (0D), subnano Pd clusters (2D or 3D) and Pd nanoparticles with crystalline phase (3D).

H₂O₂ is produced by sequential hydrogenation of O₂ on the surface, while H₂O is formed by O-O bond rupture within surface species containing O-O bond [67]. The formation of OOH and the dissociation of O₂ are key elementary steps for H₂O₂ synthesis, being responsible to the formation of H₂O₂ and H₂O, respectively. The selectivity toward H₂O₂ is therefore mainly determined by the competitive reactions between the O-H bond formation and the O-O bond cleavage. In order to evaluate the H₂O₂ selectivity over Pd/HAp models, two descriptors, R_A (the ratio of the rate constants for OOH formation and O₂ dissociation) and R_B (the ratio of equilibrium constants for OOH formation and O₂ dissociation), were calculated.

As listed in Table S2, Pd₁₀/HAp shows the highest R_A and R_B values (log(R_A) = 5.36, log(R_B) = 11.06), while log(R_A) = 2.60 and log(R_B) = 7.30 were found for Pd₃/HAp. Pd(111) presents lower R_A and R_B values (log(R_A) = -0.31, log(R_B) = -25.60) as shown in Fig. 8E and Table S2. For Pd₁/HAp, it suggests that the adsorption of H₂

is unfavorable on the single Pd site (Table S5), which hinders the subsequent H₂O₂ synthesis. It explains the inertness of Pd(I.E.) for H₂O₂ synthesis. The H₂O₂ selectivity over pure Pd₃ cluster ($\log(R_A) = -13.14$, $\log(R_B) = -44.82$) is much lower than that for Pd₃/HAp ($\log(R_A) = 2.60$, $\log(R_B) = 7.30$). The Pd₁₀ cluster also showed an inferior performance ($\log(R_A) = -7.34$, $\log(R_B) = -24.36$) compared with Pd₁₀/HAp ($\log(R_A) = 5.36$, $\log(R_B) = 11.06$). The selectivities over different Pd particles follow an order as: 3D Pd clusters > 2D Pd clusters > larger Pd particles (>2.5 nm). It is understandable that 0.5 wt % Pd, which is abundant with subnano particles, shows the highest selectivity among all catalysts.

3.5. Structure-performance relationship

H₂O₂ has proven to be formed on metallic Pd with geometric and electronic modification by additives, such as chlorine, bromide, and oxygen or nitrogen from the support [26, 33, 39, 68, 69]. However, size effects of Pd particles on H₂O₂ synthesis have rarely been reported [25]. With the combination of experiments and DFT calculations, we here envisage a structure-performance relationship by the variation of the Pd particle size.

On the basis of Pd particle sizes and catalytic performance, the catalysts studied in this work can be classified into three types (Fig. 9). The first type (Pd(I.E.)) is predominantly composed of mono-dispersed Pd atoms as evidenced by EXAFS, showing an extremely low activity due to the lack of active sites, even though single site catalysts have proven to be active for other reactions [9, 11].

The second type (0.5~2.0 wt % Pd), of which the average size of Pd particles

ranges from 1.4 nm to 2.5 nm, mainly consists of 2D and 3D Pd clusters, being responsible for H₂O₂ synthesis as identified by DFT calculations. Again, those results have proved an assertion on this reaction system: the configuration of surface Pd atoms is one of decisive factors affecting the catalytic activities [33]. Furthermore, as listed in Table 1, the structure of active sites should be modified by changing the Pd particle size in the range of 1.4~2.5 nm because the selectivity toward H₂O₂ could be significantly enhanced with the decrease in Pd particle size.

The third type (3.0~5.0 wt % Pd) mainly consists of large nanoparticles (>2.5 nm) with abundant of Pd(111) facets, which are not favorable for the formation of H₂O₂, because the metallic Pd are rather active for the O₂ dissociative activation, thus leading to the formation of H₂O. The dissociation of O₂ was detected at 200 K on the (111) facet of model Pd catalysts, and the temperature could be even lower at step and corner sites [64, 70]. It should be emphasized here that the surface configuration of Pd atoms is not unique but one of the key factors influencing the structure of active sites for H₂O₂ synthesis.

As mentioned above, we thus get a deep understanding of the Pd size effects and its structure-performance relationship for H₂O₂ synthesis. The significant effect of HAp resulted in a relatively narrow size distribution of Pd particles with average sizes ranging from ca. 1.4 nm to ca. 30 nm, leading to different geometric and electronic structures of Pd particles. In particular, a relatively high ratio of Pd^{δ+}/Pd⁰ resulted from the reaction between Pd and hydroxyls from HAp in subnano Pd particles should be the primary reason for the remarkable improvement of H₂O₂ selectivity. Pd^{δ+} in

catalysts has proved to reduce the dissociative activation of O₂ and the decomposition of H₂O₂ [33, 71]. In addition, the contraction of Pd lattice in subnano clusters with the decrease in size would lead to a concomitant weakening of chemisorptive interaction of O₂ and catalysts [72]. As a result, the Pd particles with the size of 1.4 nm (ADF-TEM) showed the maximum selectivity of 94% toward H₂O₂.

By this case study, we recognize that metal particles in subnano size are not only strongly anchored on technical catalysts, but also act as primary active sites. The structure of metal catalysts, especially the electronic structure and the chemical environment in the surface of metal particles, can be finely tailored through the control of particle size down to subnano level. At least, this work here reveals that the so-called “smaller is better” for catalysts could only be applied in a certain size range.

Nevertheless, the dynamic structure of PdO_x/Pd interfaces during the reaction is still far from clear; the effects of HAp on the formation of Pd particles are not studied; the activity still need to be improved significantly while ensuring the high selectivity remains. In particular, the effects of dimensional constrains on the catalytic performance of Pd catalysts is still ambiguous. The development of advanced separation techniques is needed to avoid excessive accumulation of H₂O₂ on the catalyst surface during the reaction, which can further improve the stability of the catalysts. The relevant studies are of great significance for the design of industrial catalysts.

4. Conclusions

As characterized by multi-techniques and experiments, size effects of Pd particles on

the catalytic performance of H_2O_2 synthesis has been demonstrated, and the selectivity toward H_2O_2 formation has found to be improved with the decrease in Pd particle size in the range of 2.5~1.4 nm, which reached to ca. 94% over 0.5 wt % Pd (d_{Pd} :~1.4 nm). In contrast, the single site catalyst (Pd(I.E.)) is inactive. The selectivity to H_2O_2 remained nearly unchanged with increasing the Pd particle size from 2.5 nm to 30 nm.

In the subnano size range, the Pd particles composed of 0D (Pd(I.E.)), 2D (0.5~2.0 wt % Pd) and 3D (0.5~5.0 wt % Pd) were observed, as identified by XRD, HRTEM and EXAFS. In the meantime, as demonstrated by XPS, in situ CO-DRIFTS and O_2 -TPD, the electronic structure of Pd surface can be tailored with varying the particle size. Especially, higher ratios of surface Pd atoms have found to be positively charged and formed PdO_x/Pd interfaces on subnano sized particles. The surface $\text{Pd}^{\delta+}$ could suppress the unexpected dissociative adsorption of dioxygen, which leads to the over-oxidation of H_2 to H_2O .

The origin of the particle size effects have been further illustrated by modeling the structures of Pd active sites using DFT calculations. Among all models, $\text{Pd}_{10}/\text{HAp}$ has found to be the optimal structure for this reaction, and subnano clusters possess the best catalytic performance. It agrees well with the experimental results. We have demonstrated that the smaller may not be better, while excellent catalytic performances could be obtained by finely optimizing the particle size in a certain range.

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Captions

Fig. 1. Time-dependent H_2O_2 synthesis over different Pd/HAp catalysts. (A) H_2 conversion. (B) H_2O_2 concentration. (C) H_2O_2 selectivity.

Fig. 2. XRD patterns of Pd/HAp catalysts. (A and B) XRD patterns of HAp and Pd/HAp catalysts with different Pd loadings. (C and D) XRD patterns of HAp (a) and 3.0 wt % Pd/HAp catalysts (b to f) under different calcination-reduction temperatures ((a) 673 K-573 K, (b) 473K-473 K, (c) 573K-573 K, (d) 673 K-573 K, (e) 773 K-573 K, (f) 873 K-573 K).

Fig. 3. Morphology of Pd/HAp catalysts. (A to E) BF-TEM images and the size distribution of the Pd catalysts with the loadings of 0.5 wt %, 1.0 wt %, 2.0 wt %, 3.0 wt %, and 5.0 wt %, respectively. (F and G) ADF-TEM images and the size distribution of the Pd catalysts with the loadings of 0.5 wt %, 1.0 wt %, respectively. (H) Aberration-corrected STEM image of the 1.0 wt % catalyst.

Fig. 4. k^2 -Weighted Fourier transform Pd K-edge EXAFS spectra of the fresh catalysts ((a) Pure PdO, (b) Pd(I.E.), (c) 0.5 wt % Pd, (d) 1.0 wt % Pd, (e) 2.0 wt % Pd, (f) 3.0 wt % Pd, (g) 5.0 wt % Pd, (h) Pd foil).

Fig. 5. In situ DRIFTS of CO adsorption over different catalysts at 283 K in an Ar flow (50 mL/min) ((a) HAp, (b) 0.5 wt % Pd, (c) 1.0 wt % Pd, (d) 2.0 wt % Pd, (e) 3.0 wt % Pd, (f) 5.0 wt % Pd).

Fig. 6. Pd3d XPS spectra of the fresh catalysts ((a) 0.5 wt % Pd, (b) 1.0 wt % Pd, (c) 2.0 wt % Pd, (d) 3.0 wt % Pd, (e) 5.0 wt % Pd).

Fig. 7. O₂-TPD profiles obtained for different catalysts in an Ar flow (50 mL/min) with a ramping rate of 20 K/min ((a) HAp, (b) 0.5 wt % Pd, (c) 1.0 wt % Pd, (d) 2.0 wt % Pd, (e) 3.0 wt % Pd, (f) 5.0 wt % Pd).

Fig. 8. Models and results of DFT calculations. (A to D) Pd₁/HAp, Pd₃/HAp, Pd₁₀/HAp, and Pd(111) models used for simulating mono-dispersed single Pd sites, two dimensional subnano Pd clusters, three dimensional subnano Pd clusters, and Pd nanoparticles with crystalline phase, respectively. Blue, red, white, purple, and green spheres are palladium, oxygen, hydrogen, phosphorus, and calcium atoms, respectively. (E) Calculating ratios of rate constants of the formation of OOH to the dissociation of O₂ (R_A) and those of equilibrium constants (R_B) over Pd₃/HAp, Pd₁₀/HAp, and Pd(111).

Fig. 9. Relations between the catalytic performance for H₂O₂ synthesis, the Pd particle sizes, and the structures of active sites. (A) Size dependence of H₂O₂ selectivity over Pd/HAp catalysts ((a)-(e): Catalysts calcined at 673 K with the Pd loadings of 0.5 wt %, 1.0 wt %, 2.0 wt %, 3.0 wt %, and 5.0 wt %, respectively; (f) 3.0 wt % Pd calcined at 773 K (Fig. S2A and Table S1); (g) 3.0 wt % Pd calcined at 873 K (Fig. S2B and Table S1)). (B) Structures of catalysts corresponding to three scales of particle sizes and proposed mechanism for H₂O₂ synthesis. Blue, red, white, purple, and green spheres are palladium, oxygen, hydrogen, phosphorus, and calcium atoms, respectively.

Table 1

Performance of Pd/HAp catalysts with different Pd loadings^a.

Catalyst	H ₂ Conversion (%)	H ₂ O ₂ Selectivity (%)	H ₂ O ₂ Productivity (mmol H ₂ O ₂ g _{Pd} ⁻¹ ·h ⁻¹)	TOF (h ⁻¹)
5.0 wt % Pd	17.8	43	741	191
3.0 wt % Pd	15.5	45	1126	269
2.0 wt % Pd	11.1	51	1378	290
1.0 wt % Pd	5.8	67	1873	340
0.5 wt % Pd	2.1	94	1857	284
Pd(I.E.)	n.d.	n.d.	n.d.	n.d.

^a Reaction conditions: 60 mL solvent (ethanol with 0.38 mL H₂SO₄), total gas flow rate of 60 mL/min (H₂:O₂:N₂=9:36:15), atmospheric pressure, 50 mg catalyst, 283 K, 1000 rpm, 0.5 h. Pd(I.E.), Pd catalyst prepared using ion-exchanging method. n.d., not determined.

Table 2

Numerical results (CNs CN, Distances R, Debye-Waller Factors σ^2) for Pd-O and Pd-Pd bonds in Pd/HAp.

Sample	Pd-O		Pd-Pd		σ^2	ΔE_0 (eV)
	R (Å)	CN	R (Å)	CN		
PdO	2.00	8	—	—	—	—
Pd (IE)	2.01±0.03	3.1±1.6	—	—	0.000±0.005	—
0.5%Pd	2.11±0.03	3.3±0.8	2.80±0.03	1.1±0.6	0.001±0.004	—
1.0%Pd	2.16±0.02	4.8±2.0	2.74±0.04	6.0±0.8	0.007±0.001	-0.5±0.8
2.0%Pd	2.06±0.02	2.2±0.7	2.73±0.01	7.7±1.1	0.007±0.001	-2.3±1.0
	2.58±0.03	3.2±1.0				
3.0%Pd	2.05±0.03	2.1±0.7	2.73±0.01	7.9±1.1	0.007±0.001	-2.2±0.9
	2.56±0.03	3.5±1.0				
5.0%Pd	2.06±0.04	1.6±0.8	2.73±0.01	8.3±1.1	0.006±0.001	-1.5±0.9
	2.58±0.04	2.5±1.0				
Pd foil	—	—	2.73	12	—	—

Figures

Fig. 1. Time-dependent H_2O_2 synthesis over different Pd/HAp catalysts. (A) H_2 conversion. (B) H_2O_2 concentration. (C) H_2O_2 selectivity.

Fig. 2. XRD patterns of Pd/HAp catalysts. (A and B) XRD patterns of HAp and Pd/HAp catalysts with different Pd loadings. (C and D) XRD patterns of HAp (a) and 3.0 wt % Pd/HAp catalysts (b to f) under different calcination-reduction temperatures ((a) 673 K-573 K, (b) 473K-473 K, (c) 573K-573 K, (d) 673 K-573 K, (e) 773 K-573 K, (f) 873 K-573 K).

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Fig. 3. Morphology of Pd/HAp catalysts. (A to E) BF-TEM images and the size distribution of the Pd catalysts with the loadings of 0.5 wt %, 1.0 wt %, 2.0 wt %, 3.0 wt %, and 5.0 wt %, respectively. (F and G) ADF-TEM images and the size distribution of the Pd catalysts with the loadings of 0.5 wt %, 1.0 wt %, respectively. (H) Aberration-corrected STEM image of the 1.0 wt % catalyst.

781

782 **Fig. 4.** k^2 -Weighted Fourier transform Pd K-edge EXAFS spectra of the fresh
 783 catalysts ((a) Pure PdO, (b) Pd(I.E.), (c) 0.5 wt % Pd, (d) 1.0 wt % Pd, (e) 2.0 wt %
 784 Pd, (f) 3.0 wt % Pd, (g) 5.0 wt % Pd, (h) Pd foil).

Fig. 5. In situ DRIFTS of CO adsorption over different catalysts at 283 K in an Ar flow (50 mL/min) ((a) HAp, (b) 0.5 wt % Pd, (c) 1.0 wt % Pd, (d) 2.0 wt % Pd, (e) 3.0 wt % Pd, (f) 5.0 wt % Pd).

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790 **Fig. 6.** Pd3d XPS spectra of the fresh catalysts ((a) 0.5 wt % Pd, (b) 1.0 wt % Pd, (c)

791 2.0 wt % Pd, (d) 3.0 wt % Pd, (e) 5.0 wt % Pd).

Fig. 7. O₂-TPD profiles obtained for different catalysts in an Ar flow (50 mL/min) with a ramping rate of 20 K/min ((a) HAp, (b) 0.5 wt % Pd, (c) 1.0 wt % Pd, (d) 2.0 wt % Pd, (e) 3.0 wt % Pd, (f) 5.0 wt % Pd).

Fig. 8. Models and results of DFT calculations. (A to D) Pd_1/HAp , Pd_3/HAp , $\text{Pd}_{10}/\text{HAp}$, and $\text{Pd}(111)$ models used for simulating mono-dispersed single Pd sites, two dimensional subnano Pd clusters, three dimensional subnano Pd clusters, and Pd nanoparticles with crystalline phase, respectively. Blue, red, white, purple, and green spheres are palladium, oxygen, hydrogen, phosphorus, and calcium atoms, respectively. (E) Calculating ratios of rate constants of the formation of OOH to the dissociation of O_2 (R_A) and those of equilibrium constants (R_B) over Pd_3/HAp , $\text{Pd}_{10}/\text{HAp}$, and $\text{Pd}(111)$.

Fig. 9. Relations between the catalytic performance for H₂O₂ synthesis, the Pd particle sizes, and the structures of active sites. (A) Size dependence of H₂O₂ selectivity over Pd/HAp catalysts ((a)-(e): Catalysts calcined at 673 K with the Pd loadings of 0.5 wt %, 1.0 wt %, 2.0 wt %, 3.0 wt %, and 5.0 wt %, respectively; (f) 3.0 wt % Pd calcined at 773 K (Fig. S2A and Table S1); (g) 3.0 wt % Pd calcined at 873 K (Fig. S2B and Table S1)). (B) Structures of catalysts corresponding to three scales of particle sizes and proposed mechanism for H₂O₂ synthesis. Blue, red, white, purple, and green spheres are palladium, oxygen, hydrogen, phosphorus, and calcium atoms, respectively.

Graphical abstract