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



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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 H₂O₂ 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 Pd²⁺/Pd⁰ 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 H₂O₂. Moreover, a sharp decrease in the reaction rates of H₂O₂ hydrogenation and direct synthesis of H₂O₂ 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.

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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

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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% H₂O₂ 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 H₂O₂ 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





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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 m²/g, pore volume 0.87 cm³/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% HNO₃, 10 wt % HNO₃, and 10 wt% HNO₃/10 wt% H₂O₂. 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 depositionprecipitation method with the anionic palladium precursor H₂PdCl₄ [40–43]. Activated carbon (1 g) suspended in deionized water was mixed with a solution of the anionic metal precursor (PdCl₂ 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(NH₃)₄(NO₃)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 HNO₃. 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 N₂/H₂ gas (50 mol% H₂, 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 N2 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 HNO₃/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) with a pass energy of 30 eV, a step increment of 0.1 eV, and an Al anode. The XPS peak positions were referenced to the carbon 1s peak at 284.6 eV. Powder X-ray diffraction (PXRD) analysis was carried out with a Rigaku diffractometer using a CuK α radiation source (40 kV and 60 mA). Transmission electron microscopy (TEM) analysis was performed using a transmission electron microscope (Philips, Tecnai G2 F30, USA).

2.5. Direct synthesis of hydrogen peroxide, natural decomposition, and hydrogenation

The direct synthesis of hydrogen peroxide from hydrogen and oxygen was carried out in a 100-mL high-pressure autoclave reactor (Büchi Picoclave, Switzerland) connected to a circulator (Julabo F25-HE, Germany). In a typical run, the catalyst (20 mg) was dried at 393 K for 4 h before use, and then introduced to the reactor with 25 g of a methanol/water mixture (80 wt% methanol) containing 20 ppm NaBr. The reactor was tightly closed, pressurized up to 30 bar with nitrogen in static mode, and evacuated to remove residual gases. The purging step was repeated twice. During the purging, the reaction temperature was adjusted to 275 K. After the purging process, the nitrogen gas in the reactor was replaced with reactant gases by co-feeding 5 mol% H₂/N₂ (30 mL/min) and 20 mol% O_2/N_2 (10 mL/min) to the reactor using two high pressure mass flow controllers (Brooks 5850E, Netherland), and the reactor was pressurized again to 30 bar with the mixed gases. After 15 min at a pressure of 30 bar, a reaction run was initiated by stirring (1200 rpm), and maintained for 0.5-2 h, typically 1 h. During the reaction, the mixed gases were continuously supplied to the reactor at a total flow rate of 40 mL/min $(H_2/O_2/N_2 \pmod{8}) =$ 3.8/5.0/91.2), and the reaction pressure was maintained using a back pressure regulator (Tescom, USA). At the end of the reaction run, the catalyst was carefully separated from the reaction product by filtration, washed thoroughly with methanol/water, and dried for further use. The amount of hydrogen peroxide produced was determined by titration with a cerium(IV) sulfate standard solution and ferroin indicator. To determine the change in hydrogen concentration during the reaction, the off-gas collected in a gas bag was analyzed with a gas chromatograph (GC, Agilent 6890, USA) equipped with a Carboxen-1010 PLOT capillary column (30 m \times 0.53 mm ID) and a thermal conductivity detector (TCD) using Ar as a carrier gas. Hydrogen conversion and selectivity were calculated according to the following equations using the hydrogen peroxide and hydrogen concentrations determined by the titration and GC analysis, respectively. The hydrogen peroxide productivity is defined as the amount of hydrogen peroxide produced per hour divided by the Pd content (mmol H₂O₂/g Pd.h).

Hydrogen Conversion (%) =
$$\frac{Moles of hydrogen reacted}{Moles of hydrogen supplied} \times 100$$

Hydrogen Selectivity (%) = $\frac{Moles of hydrogen peroxide produced}{Moles of hydrogen reacted}$

Moles of hydrogen reacted \times 100 The H₂O₂ decomposition test was carried out under the same

reaction conditions, except for the use of 1 wt% of hydrogen peroxide under nitrogen. In the H_2O_2 hydrogenation reaction, 5 mol% H_2/N_2 (30 mL/min) and N_2 (10 mL/min) gases were supplied to the reactor containing 1 wt% of hydrogen peroxide in methanol/water mixed solution. The H_2 feed-in rate was the same as that for the direct synthesis of hydrogen peroxide. The decomposed and hydrogenated hydrogen peroxide concentrations were also determined by titrating the reaction mixture.

2.6. Olefin hydrogenation

The hydrogenation of 1-decene was carried out in a liquid phase mode under atmospheric pressure. First, 20 mg of catalyst, 15 mL of 1-decene, and 15 mL of heptane were introduced to a 100-mL three-necked round bottom flask equipped with a condenser and a thermocouple. After heating to 323 K in a static mode, the reaction was started by stirring (600 rpm) with H₂ bubbling (5 mL/min) and maintained for 1 h. At the end of the reaction run, the reaction product was extracted with a syringe, filtered with a syringe filter, and analyzed with a GC (Agilent 7890A, USA) equipped with an HP-5 capillary column (30 m × 0.32 mm ID) and a flame ignition detector (FID) using N₂ as a carrier gas.

3. Results and discussion

3.1. Surface modification of activated carbon and its characterization

The characteristics of a supporting material, in particular the surface nature of the support, play a crucial role in determining the efficiency of a metal-supported catalyst. Therefore, a range of surface-modified activated carbon supports were prepared by treating activated carbon with an acid or acid/oxidant solution of different concentrations: 1 wt% HNO₃, 10 wt% HNO₃, and 10 wt% $HNO_3/10$ wt% H_2O_2 . Table S1 shows the changes in the textural properties of the activated carbon induced by the different surface treatments. The surface-modified activated carbon mostly retained its highly porous nature irrespective of the treatment conditions. A more concentrated acid treatment may increase the amount of oxygen-containing groups and enhance the acidity of the activated carbon support [47]. However, further acid treatment was not performed to avoid significant deformation of the pore structure of the activated carbon, which may impact the effect of the surface nature of activated carbon on the reaction performance.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.06.024.

Fig. 1 shows the changes in the concentration of oxygen groups and the oxygen/carbon atomic ratio of the activated carbon surface with the acid treatment process that were determined by titration and XPS analysis, respectively. The titration result indicates that the distribution and concentration of the oxygen groups on the activated carbon surface strongly depend on the treatment conditions. A small amount of lactone and hydroxyl groups were present on the untreated activated carbon surface; however, the oxygenates on the surface of the activated carbon treated with 1 wt% HNO₃ consisted of hydroxyl and carboxyl groups, and the total oxygen group concentration of the sample was ca. 11 times higher than that of the untreated one. When activated carbon was treated with 10 wt% HNO₃, the total oxygen group content was slightly reduced, but the carboxyl group content significantly increased at the expense of the reduction in the hydroxyl groups. This result suggests that the initially formed hydroxyl groups might be transformed to carboxyl groups by further reaction with the acid. In activated carbon treated with 10 wt% HNO3 and 10 wt% H2O2, the amount of hydroxyl groups slightly increased, which indicates that H₂O₂ preferentially promotes hydroxyl group formation on the activated carbon surface.

The XPS analysis also indicates that the O/C atomic ratio gradually increases with the concentration of the acid, which is consistent with the titration results, *i.e.*, a larger number of oxygen-containing groups can be incorporated on the activated carbon surface by an acid treatment of higher concentration. Although the activated carbon treated with 1 wt% HNO₃ showed the highest total oxygen group content (determined by chemical titration), the O/C atomic ratio was considerably lower than that



Fig. 1. Changes in the concentration of surface functional groups and the O/C atomic ratio of activated carbon upon acid and/or oxidant treatment.

of activated carbon treated with 10 wt% HNO_3 or 10 wt% $HNO_3/10$ wt% $H_2O_2.$

To examine the changes in the oxygen group content over the entire activated carbon domain under various acid treatment conditions, the temperature-dependent evolution of CO and CO₂ from the acid-treated activated carbon was monitored by TPD-Mass. As shown in Fig. S1(a), the two peaks observed around 850–950 K and 1000-1150 K in the CO-TPD-Mass analysis may result from the decomposition of phenol/ether and carbonyl functionalities, respectively. On the other hand, the CO₂ evolution at relatively lower temperatures (450-750 K) shown in Fig. S1(b) may be ascribed to the thermal decomposition of carboxylic groups, and the weak shoulder around 800-950 K implies the existence of carboxylic anhydrides and lactones [48,49]. The substantially reduced evolution of CO and CO₂ gases during the thermal decomposition of the 1 wt% HNO3-treated activated carbon compared to those of the activated carbon treated with 10 wt% HNO3 or 10 wt% HNO₃/10 wt% H₂O₂ clearly shows that acid treatment of higher concentration greatly increases the oxygen content of an activated carbon domain.

The DRIFTS-IR analysis presented in Fig. S2 also confirms the different distributions of the oxygen groups on the activated carbon surface with respect to the acid treatment conditions. The carbonyl (C=O) stretching band at ca. 1780 cm⁻¹ is ascribed to carboxylic acid or its anhydride form. The broad band in the range 1100–1450 cm⁻¹ may result from the C=O stretching in carboxylic acid and the lactone groups and/or from the O-H bending in the phenol groups. The peak around 1600 cm⁻¹ is attributed to the overlap between the stretching bands of polyaromatic C=C in the highly conjugated carbonyl and/or quinone groups [50,51]. The apparent peaks in these three regions, observed for the activated carbon treated with 10 wt% HNO3 and 10 wt% HNO3/10 wt % H₂O₂, clearly indicate that large amounts of carboxyl groups were newly introduced on the external surface of the activated carbon. The result closely matches the information obtained from the titration, XPS, and TPD-mass experiments.

3.2. Effect of metal deposition method on physicochemical properties of catalysts

To investigate the effect of the metal deposition method on the reaction performance of a Pd/C catalyst in the direct synthesis of hydrogen peroxide, various Pd/C catalysts were prepared using two oppositely charged palladium precursors, $[PdCl_4]^{2-}$ and [Pd

 $(NH_3)_4]^{2+}$, in combination with surface-modified activated carbon. The catalysts are listed in Table 1.

The preparation of the **Pd/C#Ax** series using the anionic palladium precursor was carried out via a conventional deposition-precipitation (**DP**) method [43,52], in which the $[PdCl_4]^{2-}$ ions were first adsorbed on the activated carbon surface, then deposited as palladium hydroxide species upon the addition of NaOH, and finally reduced by hydrogen. On the other hand, the **Pd/C#Cx** series using the cationic palladium precursor [Pd $(NH_3)_4$]²⁺ was prepared by the selective adsorption deposition (**SAD**) method. In this **SAD** method, urea was used instead of NaOH for the slow generation of hydroxide ions upon urea decomposition, which is advantageous for the gradual increase in the hydroxide ion concentration during the palladium hydroxide deposition step [45,53].

The surface charge of a support is of prime importance for the efficient and selective loading of active metal precursors on a supporting material [43,54]. Therefore, the zeta potential of the activated carbon was measured in a wide pH range before catalyst preparation, and the isoelectric point (IEP) of the activated carbon was found to be approximately pH 2.8, as shown in Fig. S3. Based on the IEP of the activated carbon support, the initial pH of the metal ion adsorption step was adjusted to 1.6 and 4 for the anionic ([PdCl₄]^{2–}) and cationic ([Pd(NH₃)₄]²⁺) precursors, respectively.

Representative transmission electron microscopy (TEM) images of the Pd/C catalysts and the changes in the Pd nanoparticle size distribution with respect to the preparation method are presented in Figs. 2–4. The formation of Pd nanoparticles was significantly affected by the metal deposition method. For example, relatively large and polydispersed nanoparticles (3–6.5 nm) were observed in the **Pd/C#Ax** series prepared by the **DP** method, but very small Pd nanoparticles (1–1.2 nm) were obtained in the **Pd/C#Cx** series regardless of the oxygen group content of the activated carbon support. This result clearly demonstrates the superiority of the **SAD** method for the formation of extremely small and monodispersed Pd nanoparticles on an activated carbon support.

The mechanism of metal deposition on activated carbon, in terms of the adsorption behavior of the palladium precursor ions and their subsequent transformation to palladium hydroxide species, should be investigated to understand the critical role of the metal deposition method on the Pd nanoparticle size and distribution, as described in Fig. 5. With the **DP** method, the initial pH of the solution was adjusted to ca. 1.6 to allow the formation of a positively charged surface; thus, the $[PdCl_4]^{2-}$ ions can be adsorbed on the activated carbon surface by chemisorption as well as physisorption, and/or ion exchange. However, during the deposition step, the pH of the solution was raised to ca. 12 by the addition of NaOH. Indeed, at high pH, the interactions between the [PdCl₄]²⁻ ions and the activated carbon support become weaker because the active carbon surface may develop a negative charge, and the non-selective adsorption of the $[PdCl_4]^{2-}$ ions may increase. In addition, the high concentration of hydroxide ions

Table 1

Pd/C catalysts with various metal precursors and surface treatments of the activated carbon support.

Metal precursor	Surface treatment of support	Catalyst
Anionic (H ₂ PdCl ₄)	Untreated 1 wt% HNO ₃ 10 wt% HNO ₃ 10 wt% HNO ₃ /10 wt% H ₂ O ₂	Pd/C#A1 Pd/C#A2 Pd/C#A3 Pd/C#A4
Cationic (Pd(NH ₃) ₄ (NO ₃) ₂)	Untreated 1 wt% HNO ₃ 10 wt% HNO ₃ 10 wt% HNO ₃ /10 wt% H ₂ O ₂	Pd/C#C1 Pd/C#C2 Pd/C#C3 Pd/C#C4



Fig. 2. TEM images of Pd/C#Ax catalysts; the insets indicate the histograms of Pd nanoparticle size.

causes the fast and heterogeneous exchange of chloride and hydroxide ligands, which results in the formation of various palladium hydroxide species including polynuclear hydroxo-palladium complexes [52]. Moreover, the nucleation and subsequent growth of palladium hydroxide in solution may be more severe because a high degree of local supersaturation of the growing nuclei is inevitable [45].

As presented in Fig. 6, the formation of palladium hydroxide was strongly affected by the pH of the solution. The dark reddish precipitate observed for all the samples (Fig. 6(a)-(f)) indicates the formation of palladium hydroxide. The precipitates turned black after reduction, which indicates the formation of Pd⁰ (not shown). The different degrees of precipitation within such a narrow pH range clearly suggest that the rate of formation of palladium hydroxide is very sensitive to the pH. The UV-vis spectra (Fig. 6(g)-(i)) show the gradual decrease and eventually the complete disappearance of the [PdCl₄]²⁻ absorption band with increasing pH, which also confirms that palladium hydroxide formation is greatly accelerated at a higher pH. Therefore, the formation of large and polydispersed palladium nanoparticles by the conventional **DP** method might be attributed to the non-selective adsorption of $[PdCl_4]^{2-}$ ions on the negatively charged activated carbon surface as well as to the rapid formation of various palladium hydroxide species at pH as high as 12.

With the **SAD** method, the use of a cationic palladium precursor $([Pd(NH_3)_4]^{2^+})$ is clearly advantageous in terms of selective and homogenous adsorption because the negatively charged activated carbon surface is maintained throughout the catalyst preparation steps. Moreover, the slow generation of hydroxides by the hydrolysis of urea not only effectively suppresses the unfavorable

nucleation of palladium hydroxide in the solution but also greatly increases the possibility of surface deposition of the selectively adsorbed $[Pd(NH_3)_4]^{2+}$ ions [45,53]. Therefore, the mechanism of the **SAD** method can be explained as follows: (i) the selective adsorption of $[Pd(NH_3)_4]^{2+}$ on the negatively charged activated carbon surface, (ii) the homogeneous surface deposition of $Pd(OH)_x$ by slow exchange of the ammonia ligands with the hydroxide ions continuously generated from urea decomposition, and (iii) the reduction of the uniformly deposited $Pd(OH)_x$ to Pd^0 . Through these processes, ultra-small and monodispersed Pd nanoparticles can be supported on an activated carbon surface.

Fig. 7 clearly shows that the amount of Pd impregnated on an activated carbon support strongly depends on the nature of the support as well as the metal deposition method. In the **Pd/C#Ax** series, similar amounts of Pd were impregnated regardless of the oxygen group content of the activated carbon support, which implies that the non-selective adsorption of $[PdCl_4]^{2-}$ ions on the negatively charged activated carbon surface was prevalent. On the contrary, the impregnated Pd content of the **Pd/C#Cx** series significantly increased as the number of oxygen groups on the activated carbon increased, and the metal loading efficiency of Pd reached 100% on the activated carbon treated with 10 wt% HNO₃/10 wt% H₂O₂. The result suggests that the Pd content on the activated carbon was determined during the initial selective adsorption of $[Pd(NH_3)_4]^{2+}$ ions on the oxygen groups of the activated carbon support.

Moreover, the carboxyl groups generated by the acid treatment were especially advantageous to increase the selective adsorption. The difference in the Pd content of the **Pd/C#Cx** series with the use of urea may imply that the deposition of non-selectively adsorbed



Fig. 3. TEM images of Pd/C#Cx catalysts; the insets indicate the histograms of Pd nanoparticle size.



Fig. 4. Pd nanoparticle size distribution based on the metal precursor and surface treatment of the activated carbon support.

palladium ions is also partially involved. However, the increasing Pd content with increasing number of carboxyl groups on the activated carbon surface clearly demonstrates that the surface deposition of the selectively adsorbed $[Pd(NH_3)_4]^{2+}$ ions is predominant. Therefore, the **SAD** method, which combines the selective adsorption of a cationic palladium precursor on a negatively charged activated carbon surface with the homogeneous formation of palladium hydroxide on the adsorbed sites, may be superior to

the conventional **DP** method in terms of the formation of extremely small and monodispersed palladium nanoparticles on the activated carbon support.

The PXRD patterns of the Pd/C catalysts are presented in Fig. S4. The broader bandwidth of the Pd [1 1 1] phase observed for the **Pd/C#Ax** series indicates the formation of larger Pd nanoparticles, which is consistent with the TEM analysis result. The [1 1 1]/[2 0 0] ratio of the Pd crystallites was measured to examine the effect of the preparation method on the crystallinity of the Pd/C catalysts. However, there was no distinguishable difference with respect to either the deposition method or the oxygen content of the activated carbon support. The Pd [1 1 1]/[2 2 0] phase ratio was not measured because the characteristic diffraction peak ca. $20 = 68^{\circ}$ overlapped with that of the activated carbon.

XPS analysis was also carried out to investigate the electronic states of Pd. The Pd(3d) region and deconvoluted chemical states of the selected Pd/C catalysts are shown in Fig. S5. The four deconvoluted peaks of $Pd(3d_{5/2})$ and $Pd(3d_{3/2})$ indicate that complete reduction was hardly achieved, regardless of the preparation method. However, the degree of reduction was significantly affected by the preparation method. For Pd/C#A1, the peak areas of Pd^0 for both the $Pd(3d_{5/2})$ and $Pd(3d_{3/2})$ regions were larger than those of Pd²⁺. On the other hand, for Pd/C#C1 and Pd/C#C4, the larger Pd^{2+} peaks of the $Pd(3d_{5/2})$ and $Pd(3d_{3/2})$ spin-orbit doublet around 337.4 and 342.8 eV (compared to the reduced Pd peaks of 335.4 eV for $3d_{5/2}$ and 340.8 eV for $3d_{3/2}$) imply that a large portion of palladium exists in an oxidized form in the Pd/C catalysts prepared by the **SAD** method. The similar Pd²⁺/Pd⁰ ratios between Pd/C#C1 and Pd/C#C4 also suggests that the oxygen content of the activated carbon surface has little impact on the reduction of



Fig. 5. Postulated mechanism for the formation of Pd nanoparticles on an activated carbon support; (a) conventional deposition-precipitation method and (b) homogeneous adsorption deposition method.



Fig. 6. Formation of palladium hydroxide under various pH conditions. Optical image at (a) pH 5.2, 0 min; (b) pH 5.2, 60 min; (c) pH 6.5, 0 min; (d) pH 6.5, 60 min; (e) pH 7.5, 0 min; and (f) pH 7.5, 60 min; UV-vis spectra at (g) pH 5.2, (h) pH 6.5, and (i) pH 7.5 (i). The experiments were carried out at 293 K under atmospheric pressure.



Fig. 7. Changes in Pd metal loading efficiency depending on the metal precursor and surface treatment of the activated carbon support (metal loading efficiency (%) = actual Pd/intake Pd \times 100).

Pd. Although Pd(OH)_x may be present, the PdO peaks (\sim 336.4 for 3d_{5/2} and \sim 341.8 eV for 3d_{3/2}) were not deconvoluted because they totally overlapped with the other peaks [55].

The difference in the electronic states of Pd with the preparation method may be attributed to the different metal deposition mechanisms. For the **DP** method, it is likely that relatively larger palladium hydroxide species may be non-selectively and rapidly deposited on the outer surface where reduction may be easier. In the **SAD** method, however, the reduction of the selectively deposited palladium hydroxide on the oxygen groups of the activated carbon surface seems more difficult.

3.3. Direct synthesis of hydrogen peroxide

The direct synthesis of hydrogen peroxide was carried out in the presence of the various Pd/C catalysts prepared by the DP and SAD methods, and the activity results are shown in Fig. 8. Both the metal deposition method and the nature of the activated carbon support played a critical role in the reaction performance of the Pd/C catalyst. The SAD method was exceptionally superior to the conventional **DP** method to obtain higher H₂ conversion rate and selectivity, and thus the productivity of Pd/C#C1 was 12 times higher than that of Pd/C#A1. According to a density functional theory (DFT) study, Pd clusters smaller than 2.5 nm may selectively catalyze H₂O₂ formation, but larger Pd nanoparticles (>2.5 nm) may preferentially promote O₂ dissociation, which results in the formation of H₂O [56]. The effect of the size of the active metal particles on the catalytic performance was also reported for supported Pd and AuPd catalysts [12,39]. Therefore, the excellent catalytic activity of Pd/C#C1 may be explained in terms of the formation of very small monodispersed Pd nanoparticles (~ 1 nm).

The nature of the activated carbon support also significantly affected the catalytic performance regardless of the catalyst preparation method. As shown in Fig. 8(b), both the H₂ conversion rate and the H₂ selectivity were greatly reduced as the oxygen group content of the activated carbon surface increased, which resulted in a significant reduction in H₂O₂ productivity (Fig. 8(a)). As there were no apparent differences in the Pd nanoparticle size and distribution upon acid treatment, it is difficult to rationalize the different catalytic activities in terms of Pd nanoparticle size. As will be discussed later, the carboxyl groups incorporated by the acid treatment may have a significant impact on the reaction performance of a catalyst in addition to the Pd nanoparticle size.



Fig. 8. Reaction performance of Pd/C catalysts in terms of (a) H_2O_2 productivity and (b) H_2 conversion rate and selectivity. Reaction conditions: catalyst (20 mg), $N_2/H_2/O_2$ (mol%) = 3.8/5.0/91.2 (30 bar), total gas flow rate = 40 mL/min, 80 wt% methanol/water solvent (25 g, 20 ppm NaBr), 275 K, reaction time = 1 h.

Higher Pd loadings on an activated carbon support bearing a large number of oxygenate groups may be responsible for the reduced catalytic activity [39,56]. However, the Pd content of **Pd/C#C3** and **C4** were higher than those of **Pd/C#A3** and **A4**, but the catalytic activity of the former was superior to that of the latter; particularly, the H₂ selectivity of **Pd/C#C4** was 9 times higher than that of **Pd/C#A4**. This result clearly demonstrates the promising aspect of the **SAD** method in realizing an efficient catalyst for the direct synthesis of hydrogen peroxide.

Fig. S6 shows the time-dependent changes in the catalytic activity of **Pd/C#C1** for the direct synthesis of hydrogen peroxide in the presence or absence of a halide additive (NaBr). In the presence of the halide ion, the initial catalytic activity was very promising: after 30 min, the H_2O_2 productivity and H_2 selectivity reached 8606 mmol H_2O_2/g Pd.h and 95.1%, respectively. As presented in Table 2, the exceptional reaction performance of the **Pd/C#C1** catalyst is comparable to that of previously reported Pd catalysts supported on various carbon materials, such as activated carbon [11,24,57], carbon nanotubes [58,59], carbon black [39], ordered mesoporous carbon [60], and carbon nanofiber [61].

As expected, although the H_2 conversion increased, the H_2O_2 productivity and H_2 selectivity significantly decreased as the reaction time was increased, regardless of the use of a halide ion. The significant reduction in both H_2O_2 productivity and H_2 selectivity is obviously attributed to the subsequent H_2O_2 decomposition and hydrogenation as well as the non-selective oxidation of H_2 to H_2O , as described in Fig. S7. The gradual increase in H_2 conversion

Table 2				
Comparison of the catalytic	c activity of Pd	I/C#C1 with recently reported Pd catalysts	supported on vario	us carbon materials.
G + 1 +	D1 (100)			F (0.6) /F (1) /F: (1)

Catalyst	Pd (wt%)	Productivity (mmol H ₂ O ₂ /g Pd.h)	H ₂ Sel. (%)	T (°C)/P (bar)/Time (h)	Additives	Ref.
Pd/C#C1 ^a	1.2	8606	95.1	2/30/0.5	20 ppm NaBr	This work
Pd/AC ^a	5	1040	42	2/40/0.5	-	[11]
Pd/N-CNT ^b	0.9	1422	45	r.t./10/1.5	250 mL H ₂ SO ₄	[58]
Pd/CB ^c	2.5	129	74	10/1/4	0.03 M HCl	[39]
Pd/CMK-3 ^d	5	5600	-	5/20/1.5	0.04 M HCl	[60]
Pd/N-CNF ^e	1	210	-	2/40/0.5	-	[61]
Pd/N-CNT ^b	0.3	140	68	r.t./30/0.33	125 mL H ₂ SO ₄	[59]
Pd/AC ^a	1	6397	54	2/30/0.25	0.03 M H ₂ SO ₄	[57]
Pd/HHDMA ^f /AC ^a	0.6	8400	80	0/40/0.5	-	[24]

^a Activated carbon.

^b Carbon nanotubes.

^c Carbon black.

^d Ordered mesoporous carbon.

^e Carbon nanofibers.

^f Hexadecyl(2-hydroxyethyl)dimethylammonium dihydrogenphosphate.

during the reaction implies that H_2 is also used in the H_2O_2 hydrogenation as well as in the direct synthesis of H_2O_2 .

The remarkably improved reaction performance with the addition of a halide ion suggests that the unfavorable non-selective oxidation of H_2 to H_2O was effectively suppressed by the halide ion. For example, the halide ion may poison the non-selective surface of Pd and thus inhibit the dissociative chemisorption of dioxygen on the palladium surface at the expense of the decrease in H_2 conversion [10]. However, the similar reduction trends in H_2 selectivity irrespective of the presence of Br^- ions implies that the gradual decrease in H_2 selectivity over time is mainly ascribed to H_2O_2 decomposition and hydrogenation rather than to the direct oxidation of hydrogen.

The use of halide ion was also advantageous to improve the reaction performance of **Pd/C#A1** catalyst. As shown in Fig. S8, the H_2O_2 productivity and H_2 selectivity were greatly increased as the amount of halide ions increased in the reaction medium. The improved catalytic activity may be resulted from the poisoning of the non-selective surface of Pd by the halide ions as supported by the sharp reduction in the H_2 conversion. The addition of halide ions showed more pronounced effect on the catalytic activity of **Pd/C#A1** compared to that of **Pd/C#C1**. In the presence of 20 ppm NaBr, the H_2O_2 productivity and H_2 selectivity of **Pd/C#A1** were 8.7 and 17.4 times higher than those obtained without NaBr. However, the volcano-shaped dependence of the catalytic activity on the halide ion content implies that there may be an optimum level for the halide ion addition and that it is difficult to overcome the low activity of **Pd/C#A1** catalyst solely by the addition of NaBr.

To investigate the important role of the selective adsorption of a palladium ion on the activated carbon support in determining the catalytic activity, another Pd/C catalyst was prepared via the SAD method using the anionic palladium precursor, H₂PdCl₄ (Anionic/ SAD Pd/C). As shown in Fig. S9, not only the palladium precursor types but also the catalyst preparation methods exerted crucial effect on the characteristics of Pd nanoparticles. The relatively smaller Pd nanoparticles $(3.3 \pm 0.6 \text{ nm})$ of the Anionic/SAD Pd/C than those of the Pd/C#A1 (4.8 ± 1.5 nm) implies that the gradual generation of hydroxide ions by urea decomposition is advantageous in terms of the control of nanoparticle size. However, the similar electronic nature of the Anionic/SAD Pd/C with that of the **Pd/C#A1** (low Pd²⁺/Pd⁰ ratio) suggests that the palladium hydroxide species formed by the ligand exchange of the non-selectively and weakly adsorbed [PdCl₄]²⁻ ions may be easily reduced regardless of the preparation methods.

The activity test of the Anionic/SAD Pd/C catalyst is presented in Fig. S10. The H_2O_2 productivity and H_2 selectivity of the Anionic/SAD Pd/C catalyst were found to be 589 mmol H_2O_2/g Pd.h and

22%, respectively. The low activity of the Anionic/SAD Pd/C catalyst may be understood in terms of the formation of large Pd nanoparticles with low Pd²⁺/Pd⁰ ratio as similar as those of **Pd/C#A1**. The result clearly confirms that selective adsorption of the cationic palladium ions on the negatively charged activated carbon surface is of prime importance for the formation of very small and monodispersed Pd nanoparticles with a high Pd²⁺/Pd⁰ ratio, and thus for attaining high catalytic activity for the direct synthesis of hydrogen peroxide.

3.4. Hydrogen peroxide decomposition and hydrogenation

One of the challenging issues in the direct synthesis of hydrogen peroxide is that all the reaction pathways are thermodynamically favorable, and the active metal, such as Pd, may catalyze H_2O_2 formation as well as its subsequent decomposition and hydrogenation. Therefore, the reaction performance of a catalyst for the direct synthesis of hydrogen peroxide may be determined by the combination of its activities for these reactions. In this context, the activity of the Pd/C catalysts in the decomposition and hydrogenation of H_2O_2 was examined. As shown in Fig. 9, both the H_2O_2 decomposition and hydrogenation rates were greatly affected by the metal deposition method and the nature of the activated



Fig. 9. H_2O_2 decomposition and hydrogenation in the presence of Pd/C catalysts prepared with different metal precursors and/or surface treatment methods of the activated carbon support. Reaction conditions: catalyst (20 mg), 1 wt% H_2O_2 in 80 wt% methanol/water solvent (25 g, 20 ppm NaBr), 30 bar, 275 K, reaction time = 1 h. Gas flow rate for H_2O_2 decomposition = 40 mL/min (N₂). Gas flow rate for H_2O_2 hydrogenation = 30 mL/min (5 mol% H_2/N_2) and 10 mL/min (N₂).

carbon support, but showed opposite trends based on the nature of the activated carbon support regardless of the metal deposition method.

The **Pd/C#Ax** catalyst showed H_2O_2 decomposition rates 6.6–12.1 times higher than those of **Pd/C#Cx**, which may be due to the higher Pd⁰/Pd²⁺ ratio of the **Pd/C#Ax** catalysts, as observed in the XPS analysis. In addition, various AuPd catalysts with higher Pd⁰/Pd²⁺ ratios showed lower H_2 selectivity owing to their ability to accelerate the unfavorable H_2O_2 decomposition [27,62,63]. The Pd nanoparticle size also affects the H_2O_2 decomposition rate, and larger Pd nanoparticles (>2.5 nm) have a lower H_2 selectivity because of faster H_2O_2 decomposition [56]. Therefore, the faster H_2O_2 decomposition rate with the **Pd/C#Ax** series may be ascribed to the presence of relatively larger Pd nanoparticles with higher Pd⁰/Pd²⁺ ratios.

Another interesting aspect of the experiment is the increase in the H_2O_2 decomposition rate with the oxygen content of the activated carbon surface, especially carboxyl groups, regardless of the catalyst preparation method. The natural breakdown of H₂O₂ increases as the hydrophilicity of the surface increases, and thus, a hydrophobic surface is beneficial to prevent H₂O₂ decomposition [10,64–66]. Therefore, the enhanced hydrophilicity of an activated carbon surface from the incorporation of various oxygenates may be responsible for the faster H₂O₂ decomposition rates. Although there are no apparent difference in the total amount of oxygen groups on the activated carbon surface treated with different acid concentrations, as shown in the titration experiment (see Fig. 1), the faster H₂O₂ decomposition rates over Pd/C#C3 and #C4 compared to Pd/C#C2 suggest that the carboxyl groups have a larger influence on the formation of a hydrophilic surface than the hydroxyl groups.

The weak electrolytic nature of carboxyl groups may be responsible for the increased H_2O_2 decomposition rate on a hydrophilic activated carbon surface. In the presence of a strong electrolyte such as H_2SO_4 , H_2O_2 decomposition can be effectively suppressed because the H-OOH dissociation may be retarded by the excess protons [1,10,31,32,67]. With carboxylic acid, the hydrogen bonds between the carboxyl groups and H_2O_2 may accelerate H_2O_2 hydrolysis to H_2O , which may offset the benign effect of the protons on the suppression of H-OOH dissociation.

Contrary to H₂O₂ decomposition, the H₂O₂ hydrogenation rate decreased as the number of oxygenates on the activated carbon increased. In particular, the reduction in the H₂O₂ hydrogenation rate was much larger for the Pd/C#Cx series than the Pd/C#Ax series. The steep decrease in the H₂O₂ hydrogenation rate is very similar to the rapid decrease in the reaction rate of the direct synthesis of H_2O_2 in the presence of the same catalyst, which suggests that the carboxyl groups near the Pd nanoparticles may have a detrimental effect on both reactions. It is assumed that the carboxyl groups near the active Pd metal sites may act as poison for the active sites and/or restrict the reactants' access to the active sites. In the **Pd/C#Cx** series, the undesirable influence of the carboxyl groups on the catalytic activity is more prominent because the ultra-small Pd nanoparticles are located in close proximity to the carboxyl groups on the activated carbon surface, which resulted in a sharp decrease in reaction rates compared to the Pd/C#Ax series in which larger and polydispersed Pd nanoparticles mainly exist on the outer surface [43,52]. A similar negative effect of carboxyl groups on reaction performance has been reported [39]. Vannice and coworkers also reported that carbon might contaminate bulk and surface Pd and therefore suppress chemisorption on the Pd surface [38]. Considering the increase in the H₂O₂ decomposition rate as the number of carboxyl groups increases, the carboxyl groups has little impact on the intrinsic catalytic activity of Pd for H₂O₂ decomposition. However, increasing the number of carboxyl groups on an activated carbon surface may decrease H_2 selectivity by enhancing the hydrophilic nature of the support and/or by promoting H_2O_2 hydrolysis. In this regard, the carboxyl groups may retard H_2O_2 formation and hydrogenation by poisoning the active sites rather than by restricting the access of the reactants to the active sites.

3.5. Effect of the surface nature of the activated carbon support on the reaction performance

To clarify the influence of the carboxyl groups of the activated carbon support on the catalytic activity, the direct synthesis of hydrogen peroxide over Pd/C#C1 was carried out in the presence of sulfuric or acetic acid. To maintain a constant concentration of protons, the pH was kept at 3.5 regardless of the acid additive used. As shown in Fig. 10, when sulfuric acid was introduced, the increased number of protons effectively suppressed H₂O₂ decomposition, and both the H₂O₂ productivity and H₂ selectivity increased while H₂ conversion remained constant. On the other hand, with the addition of acetic acid, H₂ conversion and selectivity decreased, which resulted in a significant reduction in H₂O₂ productivity. The H₂ conversion gradually increased with reaction time because of the consumption of hydrogen in the subsequent H₂O₂ hydrogenation; however, the observed reduction in H₂ conversion upon addition of acetic acid indicates that the catalyst partially lost its activity. Moreover, the simultaneous decrease in H₂ conversion and selectivity implies that acetic acid may also promote H_2O_2 hydrolysis. Although the decreased H_2 conversion is attributed to the poisoning of the Pd active sites by acetic acid, the reduced H₂ selectivity is mainly ascribed to the enhanced H₂O₂ decomposition rather than to poisoning.

To further confirm the poisoning effect of the carboxyl groups of the activated carbon surface on the catalytic activity, hydrogenation of 1-decene was carried out using the **Pd/C#Ax** and **Pd/C#Cx** catalysts. As shown in Fig. 11, the reaction performance strongly depends on both the metal deposition method and the surface nature of the support, and the reduction in the catalytic activity of the **Pd/C#Cx** series was more significant than that of **Pd/C#Ax**.

The changes in the reaction performance of these catalysts for olefin hydrogenation follow the same trend as that for the direct synthesis and hydrogenation of hydrogen peroxide. The result clearly demonstrates that the carboxyl groups near Pd may noticeably exert a detrimental effect on the catalytic activity by hindering or poisoning the active sites. The negative influence of the carboxyl groups on the active sites in combination with the unfavorable acceleration of H_2O_2 hydrolysis by the formation of



Fig. 10. Changes in the catalytic performance of Pd/C#C1 in the presence of different acids.



Fig. 11. Effect of surface treatment of Pd/C catalysts on hydrogenation of 1-decene.



Fig. 12. Illustration of the unfavorable effect of carboxyl groups in accelerating H_2O_2 hydrolysis as well as hindering or poisoning the active metal sites.

hydrogen bonds with H_2O_2 resulted in a significant reduction in the catalytic performance as the amount of carboxyl groups on the activated carbon support increased, as described in Fig. 12.

3.6. Catalyst recycling

The catalyst recyclability was also tested by repeated reaction cycles using **Pd/C#C1** under the same reaction conditions. The catalyst was carefully filtered at the end of each reaction cycle. The recovered catalyst was washed thoroughly with water and methanol, dried overnight at 383 K, and then reused. As shown in Fig. S11, the activity of the recycled catalyst diminished slightly, but after the third recycle run, the catalytic activity was maintained. It seems that that the reduced activity of the recycled catalysts may be caused by the partial leaching of Pd during the first reaction or recycle step. Sintering of Pd nanoparticles or accumulation of halide ions on the palladium surface as a reason for the deactivation can be excluded because the H₂O₂ productivity as well as H₂ selectivity was maintained during the recycle runs.

4. Conclusion

An efficient Pd/C catalyst design for the direct synthesis of hydrogen peroxide was realized by the selective adsorption deposition method, in which a cationic palladium precursor such as $[Pd(NH_3)_4]^{2+}$ was selectively adsorbed on a negatively charged activated carbon surface and subsequently converted to palladium hydroxide in a homogeneous manner with hydroxide ions that were slowly generated upon urea decomposition. The formation

of ultra-small and monodispersed Pd nanoparticles with a high Pd^{2+}/Pd^{0} ratio resulted in one of the highest reaction performances among previously reported Pd catalysts supported on various carbon materials. The high initial H₂O₂ productivity and H₂ selectivity of 8606 mmol H₂O₂/g Pd.h and 95.1%, respectively, were achieved in the presence of the **Pd/C#C1** catalyst after 30 min under intrinsically safe and non-corrosive conditions. The excellent H₂O₂ productivity and H₂ selectivity of the **Pd/C#C1** catalyst prepared by the selective adsorption deposition method were 12 and 7.1 times higher, respectively, than those of the **Pd/C#A1** catalyst prepared by a conventional deposition-precipitation method.

In addition, the oxygen groups, particularly the carboxyl groups, of the activated carbon surface, which were incorporated by acid treatment, have a huge impact on the reaction performance of the catalyst, regardless of the preparation method. Increasing the number of carboxyl groups on the activated carbon surface may lead to the acceleration of H₂O₂ decomposition. As confirmed by the acid addition experiment, H₂O₂ decomposition can be effectively suppressed in the presence of a strong electrolyte such as H₂SO₄. However, carboxylic acid, which is a weak electrolyte, does not effectively suppress H-OOH dissociation but rather promotes H₂O₂ hydrolysis by forming hydrogen bonds with H₂O₂. Furthermore, the sharp decrease in the direct synthesis and hydrogenation rates of H₂O₂, as observed in olefin hydrogenation experiments, suggests that the carboxyl groups near the active sites exert a negative influence on the catalytic activity by hindering or poisoning the active sites. These detrimental effects of the carboxyl groups may be responsible for the significant reduction in the reaction performance of catalysts as the carboxyl group content of the activated carbon support increases.

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