Palladium Catalysts Supported on Mesoporous Carbon for Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen

수소와 산소로부터 과산화수소를 직접 제조하기 위한 중형기공성 탄소에 담지된 팔라듐 촉매

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Abstract

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Hydrogen peroxide has been considered as a powerful oxidant in various industries, because it possesses strong oxidizing ability and it can be used without generating harmful by-products. Although hydrogen peroxide has been commercially produced by anthraquinone auto-oxidation process for several decades, this process has severe drawbacks such as the environmental problem and cost-effectiveness issue. Therefore, direct synthesis of hydrogen peroxide from hydrogen and oxygen has attracted much attention as one of the promising processes to replace the anthraquinone auto-oxidation process. Palladium-based noble metal was found to be effective for this reaction. However, low selectivity for hydrogen peroxide still remains unsolved due to
simultaneously occurring side reactions. Liquid acids and halides have been used as additives to improve the selectivity of hydrogen peroxide in the direct synthesis of hydrogen peroxide. However, the strong acid additives in reaction medium causes the dissolution of active metal from supported catalyst and the corrosion of reactor. Therefore, the acidic support have been applied to the direct synthesis of hydrogen peroxide to diminish the amount of liquid acid additives.

In this work, shape-controlled palladium nanocube particles were employed for the direct synthesis of hydrogen peroxide to investigate the size effect of palladium particles on the catalytic performance. Then, palladium catalysts supported on acidic solid supports were employed for the direct synthesis of hydrogen peroxide in the absence of acid additives. The effect of acidic solid supports on the catalytic performance of the catalysts in the direct synthesis of hydrogen peroxide was investigated. A correlation between property of acidic supports and catalytic performance of the catalysts was elucidated.

Size-controlled palladium (Pd) nanocubes were prepared by colloidal methods in the presence of different surface-stabilizing agents, polyvinylpyrrolidone (PVP) and tetradecyltrimethylammonium bromide (TTAB). Average particle sizes of PVP-stabilized Pd nanocubes were 12, 15, and 18 nm (denoted as PVP-XPC (X = 12, 15, and 18)). In case of TTAB-stabilized Pd nanocubes, average particle sizes were 18, 25, and 33 nm (denoted as TTAB-XPC (X = 18, 25, and 33)). The Pd nanocubes supported on \(\gamma\)-Al\(_2\)O\(_3\) were applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Conversion of hydrogen and selectivity for hydrogen
peroxide increased with decreasing size of Pd nanocubes. The effect of stabilizing agent was also investigated by comparing the catalytic activity of Pd nanocubes prepared with different stabilizing agent. TTAB-stabilized Pd nanocubes showed better catalytic activity than PVP-stabilized Pd nanocubes. FT-IR and TGA analyses revealed that strong C=O and C-N chemical bonding species remained on the PVP-stabilized Pd nanocubes, while only a small amount of alkyl species remained on the TTAB-stabilized Pd nanocubes. This different catalytic activity of Pd nanocubes was due to the difference in remaining chemical species on the Pd surface between PVP- and TTAB-stabilized nanocubes.

A series of palladium catalysts supported on the ordered mesoporous carbon (denoted as Pd/OMC-T) were prepared by surfactant-templating and incipient wetness impregnation method with a variation of precursor solution temperature (T = 8, 15, 25, 35, 45 °C) during the synthesis of OMC. Prepared catalysts were applied to direct synthesis of hydrogen peroxide from hydrogen and oxygen in the presence of halide and acid additives (NaBr and H₂SO₄). The effect of synthesis temperature on the physicochemical properties and catalytic activities of Pd/OMC-T catalysts in the direct synthesis of hydrogen peroxide was investigated. Conversion of hydrogen and yield for hydrogen peroxide over Pd/OMC-T catalysts showed volcano-shaped trend with respect of the precursor solution temperature. The catalytic performance was found to be closely related to palladium surface area and growth of the specific crystal phase.
In order to exclude the strong liquid acid additive, another series of palladium catalysts supported on the heteropolyacid-containing ordered mesoporous carbon (denoted as Pd/OMC-XHPA) was prepared by incipient wetness impregnation and ion-exchanging method with different HPA contents (X = 5, 10, 20, 30, 40 wt%). Prepared catalysts were applied to direct synthesis of hydrogen peroxide in the absence of acid additive. Selectivity and yield for hydrogen peroxide showed volcano-shaped curve with increasing the HPA content. The effect of different HPA content on the physicochemical properties and surface acidity of the catalysts was investigated. The pore structure of OMC was maintained after loading the HPA and palladium. However, aggregate of HPA was formed in the catalysts with higher HPA loading. The acidity of Pd/OMC-XHPA catalyst also showed volcano-shaped trend with increasing the HPA content. The superior catalytic performance of Pd/OMC-20HPA catalyst was due to its high surface acidity. Therefore, it was concluded that the improved catalytic performance for direct synthesis of hydrogen peroxide was achieved by controlling surface area of carbon support and enhancing the surface acidity of catalyst.

A series of ordered mesoporous carbon (OMC) were sulfonated by a covalent attachment of sulfonic acid-containing aryl radical with a variation of sulfonating agent (4-benzenediazonium sulfonate)/OMC ratio (X) (denoted as OMC-S-X, X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25, weight ratio). Palladium catalysts supported on OMC-S-X were prepared by an incipient
wetness impregnation method (denoted as Pd/OMC-S-X). Pd/OMC-S-X catalysts were then employed for direct synthesis of hydrogen peroxide from hydrogen and oxygen in the absence of acid additive. The effect of sulfonating agent ratio on the physicochemical properties and catalytic activities was investigated. Cylindrical mesoporous structure and uniformly dispersed palladium were retained in all the catalysts. Catalytic activity in the direct synthesis of hydrogen peroxide over Pd/OMC-S-X showed a volcano-shaped trend with respect to the ratio of sulfonating agent. Reducibility of the Pd/OMC-S-X catalysts was closely related to the catalytic performance. It was revealed that selectivity for hydrogen peroxide increased with increasing reduction temperature of the catalyst, indicating that oxidized state of palladium played a significant role in improving catalytic activity in this reaction. Among the catalysts tested, Pd/OMC-S-0.125 with the highest reduction temperature showed the highest selectivity for hydrogen peroxide.

In summary, palladium nanoparticles and palladium supported on acidic supports such as heteropolyacid-introduced and sulfonated ordered mesoporous carbon were prepared, and they were applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. The catalysts were characterized by nitrogen adsorption-desorption, FT-IR, XRD, CO chemisorption, TEM, TPR, and NH₃-TPD analyses.

**Keywords:** Hydrogen peroxide, Hydrogen, Oxygen, Palladium catalyst, Ordered-mesoporous carbon, Acidic support

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Chapter 1. Introduction

1.1. Hydrogen peroxide

Hydrogen peroxide is widely used in various areas such as pulp industry, pharmaceutical industry, water treatment, and chemical synthesis, due to its strong oxygen donating ability and environmentally benign nature [1,2]. Due to its low molecular weight, active oxygen content of hydrogen peroxide (47.1%) is higher than other oxidants such as tertiary butyl hydroperoxide (t-BuOOH, 17.8%), sodium hypochlorite (NaClO, 21.6%) and nitric acid (HNO₃, 25.0%). When hydrogen peroxide is used as an oxidant in reactions, produced by-product is solely water, so it is called green oxidant. Market for hydrogen peroxide is expected to increase especially in chemical industries in the near future, because the process for production of propylene oxide using hydrogen peroxide as an oxidant has been developed, which is called hydrogen peroxide-propylene oxide (HPPO) process [3,4].

At present, hydrogen peroxide is commercially produced through anthraquinone auto-oxidation process. The anthraquinone auto-oxidation process was initially introduced in Germany in the 1940s, and all succeeding hydrogen peroxide plants were based on this process. In the anthraquinone process hydrogen does not directly contact with oxygen, resulting in safe reaction conditions [5]. However, the anthraquinone process requires complex synthesis and purification steps, accompanying with usage of expensive organic materials and massive amount of organic solvents. This demerit of
anthraquinone process results in the economical limitation and environmental issues \[6,7\]. With these increasing concerns on environment and cost-effectiveness, there had been many efforts to replace the commercial anthraquinone process.
1.2. Direct synthesis of hydrogen peroxide

Direct synthesis of hydrogen peroxide from hydrogen and oxygen has been suggested as an alternative for anthraquinone process, because it suggests a promising way to remedy environmental and economical demerits of anthraquinone oxidation process [8,9]. Due to simple reaction pathway and production process, direct synthesis of hydrogen peroxide can be implemented at the site of use [10,11]. In spite of pollutant-free and cost-effective benefits, there are drawbacks to overcome for commercializing direct synthesis process of hydrogen peroxide. Direct synthesis of hydrogen peroxide and involved reactions are shown in Figure 1.2. The target reaction forming hydrogen peroxide (Reaction I) involves adsorption of reactant molecules (hydrogen and oxygen), rearrangement of hydro-peroxy bonds, and desorption of produced hydrogen peroxide. Major problems are simultaneous formation of water (Reaction II) with hydrogen peroxide, consecutive decomposition and hydrogenation of hydrogen peroxide to water (Reaction III, IV) [12]. All these related reactions are thermodynamically favorable and highly exothermic. Particularly both formation of water (Reaction II) and hydrogenation of hydrogen peroxide (Reaction IV) are thermodynamically more favorable than the synthesis of hydrogen peroxide. As a consequence, selectivity for hydrogen peroxide in the direct synthesis of hydrogen peroxide is deteriorated by these unwanted reactions, leading to low productivity for hydrogen peroxide.
Fig. 1.1. Reactions involved in the direct synthesis of hydrogen peroxide from hydrogen and oxygen.
1.3. Selective formation of hydrogen peroxide

As mentioned in previous section (Section 1.2), yield for hydrogen peroxide is limited in the direct synthesis of hydrogen peroxide, due to undesired side reactions: non-selective oxidation of hydrogen to water, hydrogenation of hydrogen peroxide, and decomposition hydrogen peroxide. In order to solve this problem, there have been many investigations to increase the selectivity for hydrogen peroxide in the direct synthesis of hydrogen peroxide. Precious metals such as palladium, platinum, gold, and their bimetallic combinations have been studied as active species in this reaction for efficient catalyst design [13-17]. Among the catalysts, palladium-based mono- and bi-metallic catalysts showed remarkable catalytic activity on different supports [13-16]. However, metal catalyst, by itself, is also active for the unwanted reactions lowering the hydrogen peroxide selectivity. Therefore, there have been efforts to deter the activity of catalysts for side reactions maintaining the activity for target reaction. It was known that formation of water and decomposition of hydrogen peroxide can be suppressed by using liquid acid and halide additives in reaction medium [15,18]. Especially, Br- and Cl- ions are widely used as suppressing additives. The effect of halide ions in the direct synthesis of hydrogen peroxide is due to the selective blocking of metal surface active for the undesired side reactions. However, excessive addition of halide ions caused the poisoning of active metal, leading to inhibition of hydrogen conversion and reduced yield of hydrogen peroxide [21].
Liquid acids are also employed in the reaction medium to increase the productivity of hydrogen peroxide [22,23]. Positive effect of acid is known to be responsible for inhibiting the decomposition of hydrogen peroxide by reducing the dissociative hydrogen peroxide decomposition [24,25]. However, the presence of strong acid and halide additives in reaction medium causes the dissolution of active metal from supported catalyst and the corrosion of reactor, which is the critical obstacle for commercialization. There have been studies for utilizing acidic supports as alternative acid source to overcome this obstacle [19,20].

1.3.1. Nanoparticles

Synthesis of nanoparticles has attracted much attention due to their unique characteristics and variety of potential applications. The characteristics of metal nanoparticles are determined by their physical parameters such as structure, shape, composition and size. The properties can be controlled by tailoring those parameters [26]. There are various applications for metal nanoparticles such as medicine, electronics, photonics, sensing, and catalysis [26-28]. For catalysis, it is widely known that catalytic performance influenced with the decrease of particle size due to high surface to volume ratio. Furthermore, selectivity was affected by its structure [29]. It has been reported that precious metal nanoparticle (Au, Pt, Pd and Ag) with different size and structure (cube, rod, octahedron, tetrahedron, and etc.) are successfully synthesized, showing unique properties in catalysis [30-32].
1.3.2. Ordered mesoporous carbon (OMC)

Carbon is a promising material as a support for catalysis applications due to the modifiability of its physicochemical properties such as surface area, acidity, hydrophobicity, etc. Particularly, porous nature of carbon materials facilitates its use of applications such as electrochemical storage, water purification, capacitors and gas separation. Porous carbons are classified as microporous (pore size < 2 nm), mesoporous (2-50 nm), and macroporous (> 50 nm) carbon according to their pore size. It is known that mesoporous carbon materials such as ordered mesoporous carbon and CMK carbons showed superior catalytic performances than activated carbon with micropores for the catalytic reaction operated in mass transfer limitations. Thus, ordered mesoporous carbon is potentially available as a supporting material due to controllable textural properties, uniform pore structure, and efficient mass transfer of reactants [35-36]. These unique properties make OMC well suited as a potential candidate material for catalyst support.

1.3.3. Acidic solid supports

Heteropolyacids (HPA) are inorganic acids. It is known that acidity of heteropolyacid is stronger than that of other solid acids. Thus, heteropolyacid has been applied as a solid acid catalyst in various acid-catalyzed reactions [37,38]. Although heteropolyacid is highly soluble in polar solvents, it has been reported that insoluble heteropolyacid with high surface area can be
prepared by ion exchange with large cations [39,40]. It has also been reported that acidity of insoluble heteropolyacid can be controlled by changing the content of exchanging cations [41]. Therefore, it is expected that introduction of heteropolyacid into supporting materials makes the catalyst possess strong acidity as solid acid for direct synthesis of hydrogen peroxide.

On the other hand, sulfonated mesoporous materials are well-known to have excellent acid property [42-44]. It has been reported that degree of sulfonation differs on the sulfonation method and sulfonating conditions [45,46]. And the acidity of mesoporous support is determined by the degree of sulfonation. Thus, it is expected that sulfonated carbon materials with different degree of sulfonation will show diverse acidity and physicochemical properties, resulting in different ability for direct synthesis of hydrogen peroxide.
Chapter 2. Experimental

2.1. Preparation of catalysts

2.1.1. Preparation of palladium nanoparticle catalysts

Two different types of surface-stabilizing agents were utilized for the preparation of palladium nano-cubes. PVP-stabilized palladium particles were prepared according to the methods in the literature [47]. Typical procedures for the preparation of PVP-stabilized palladium particles are as follows. 0.24 mmol of PVP (Sigma-Aldrich) and a known amount of sodium bromide (NaBr, Samchun chemicals) were dissolved in 20 ml of deionized water at room temperature, and it was heated at 80 °C for 30 min. 7.5 ml of aqueous solution containing 0.48 mmol of K₂PdCl₄ (Sigma-Aldrich) and 0.85 mmol of L-ascorbic acid (Samchun chemicals) was then added to the solution. The mixture with dark grey precipitates was maintained at 80 °C for 3 h under stirring. The resulting mixture was mixed with acetone in the volume ratio of 1 (mixture) : 5 (acetone). Palladium nanoparticles were separated by centrifuging the mixture at 10,000 rpm for 10 min. The separated nanoparticles were washed with deionized water several times. The prepared PVP-stabilized palladium nanocubes with a particle size of 12, 15, and 18 nm were denoted as PVP-XPC (X = 12, 15, and 18), where X represented the particle size in nanometer.
For the preparation of TTAB-stabilized palladium nanoparticles, a known amount of TTAB (Sigma-Aldrich) was dissolved in 100 ml of deionized water at 90 °C. 5 ml of K₂PdCl₄ aqueous solution was quickly added into the solution under stirring, and it was kept for 30 min. L-ascorbic acid solution (0.1 M) was then added dropwise into the precursor solution. After maintaining the solution at 90 °C for 1 h, ethanol was added to the mixture in the volume ratio of 1 (mixture) : 3 (ethanol). The mixture was further stirred for 3 h. The mixture containing black precipitates was kept at room temperature for 5 h. The prepared palladium nanoparticles were separated by centrifuging the mixture at 10,000 rpm for 10 min, and they were washed with ethanol several times. The prepared TTAB-stabilized palladium nanocubes with a particle size of 18, 25, and 33 nm were denoted as TTAB-XPC (X = 18, 25, and 33), where X represented the particle size in nanometer.

Palladium nanoparticle catalysts were employed in the direct synthesis of hydrogen peroxide as-prepared and catalysts supported on alumina. The supported catalysts were prepared by a wet impregnation method using palladium nanoparticles and alumina (γ-Al₂O₃, surface area=220 m²/g, pore volume = 0.62 cm³/g, Alfa Aesar). The nanoparticles were re-dispersed in ethanol by sonication to obtain a nanoparticle colloid, and a known amount of alumina powder was added to palladium colloid under vigorous stirring. The slurry was then dried in a vacuum oven overnight at 80 °C. The palladium loading was fixed at 2.5 wt% for all samples. The prepared catalysts were denoted as PVP-XPC/Al₂O₃ (X = 12, 15, and 18) and TTAB-XPC/Al₂O₃ (X = 18, 25, and 33).
Fig. 2.1.1. Schematic procedures for the preparation of palladium nanoparticle catalysts.
2.1.2. Preparation of palladium catalysts supported on ordered mesoporous carbon

Carbon supports can be prepared by several methods such as surfactant-templating method and RF polymerization method. In particular, pore size and pore structure of carbon support can be controlled by selecting different surfactant or by changing preparation conditions. In this work, ordered mesoporous carbon supports (denoted as OMC-T, T = 8, 15, 25, 35, and 45 °C) were prepared by a surfactant-templating method using P123 and TEOS as templates according to the similar methods reported in the literature [36]. (EO)$_{20}$(PO)$_{70}$(EO)$_{20}$ triblock copolymer (Pluronic P123, Sigma-Aldrich) was dissolved in HCl solution (450 ml) at different temperature (8, 15, 25, 35, and 45 °C) with constant stirring for 4 h. Carbon precursor material (Sucrose, TCI) and H$_2$SO$_4$ solution were added into the solution under vigorous stirring for 1 h. Silica template precursor (Tetraethyl orthosilicate, Sigma-Aldrich) was slowly added into the solution. After stirring the mixture for 24 h, it was maintained at 100 °C for 20 h under static condition. The mixture was dried at 100 °C for 48 h, and then carbonized at 800 °C for 4 h at a heating rate of 5 °C/min under a nitrogen flow (100 ml/min). Carbon-silica composite was treated with 5 wt% HF solution to remove silica template. Ordered mesoporous carbon (OMC) was finally obtained after washing, filtering, and drying the resultant.

Palladium was supported on OMC-T (T = 8, 15, 25, 35, and 45 °C) by an incipient wetness impregnation method. Palladium chloride (PdCl$_2$, Sigma-
Aldrich) was dissolved in acetone containing 0.1 M HCl, and it was introduced into the pores of OMC-T. Palladium loading was fixed at 2.5 wt% for all samples. After drying the impregnated sample overnight at 80 °C, it was calcined at 300 °C for 3 h under a nitrogen flow. The supported catalysts were then reduced at 200 °C in a mixed stream of hydrogen (2.5 mL/min) and nitrogen (47.5 mL/min) for 4 h. The prepared catalysts were denoted as Pd/OMC-T (T = 8, 15, 25, 35, and 45 °C), where T represented the preparation temperature of ordered mesoporous carbon in Celcius.
Fig. 2.1.2. Schematic procedures for the preparation of palladium catalysts supported on ordered mesoporous carbon (Pd/OMC-T, T = 8, 15, 25, 35, and 45 °C).
2.1.3. Preparation of palladium catalysts supported on heteropolyacid-containing ordered mesoporous carbon

Heteropolyacid-containing ordered mesoporous carbon support was prepared by incipient wetness impregnation and ion exchange method. A known amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Sigma-Aldrich) was impregnated onto ordered mesoporous carbon (OMC-25) by an incipient wetness impregnation method. The impregnated sample was dispersed in 10 ml of ethanol containing cesium chloride (CsCl, Sigma-Aldrich), and the mixture was stirred for 12 h for ion exchange. The collected solid was dried overnight at 80 °C after filtering and washing. Cesium content was controlled to be $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ for all samples in order to take advantage of high surface acidity of heteropolyacid [12,13]. The solid was calcined at 300 °C for 3 h under a nitrogen flow to obtain OMC-XHPA ($X = 5, 10, 20, 30, \text{ and } 40 \text{ wt%}$).

2.5 wt% of palladium was supported on OMC-XHPA by an incipient wetness impregnation method. The detailed procedures were the same as mentioned in section 2.1.2. The prepared catalysts were denoted as Pd/OMC-XHPA ($X = 5, 10, 20, 30, \text{ and } 40 \text{ wt%}$), where $X$ represented the content of heteropolyacid ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$) in ordered mesoporous carbon.
Fig. 2.1.3. Schematic procedures for the preparation of palladium catalysts supported on heteropolyacid containing ordered mesoporous carbon (Pd/OMC-XHPA, X = 5, 10, 20, 30, and 40 wt%).
2.1.4. Preparation of palladium catalysts supported on sulfonated ordered mesoporous carbon

A series of Pd/OMC-S-X catalysts (X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25) were prepared by a surfactant-templating method, a sulfonation method, and a subsequent incipient wetness impregnation method. For the preparation of mesoporous carbon support, 20 g of triblock copolymer (EO)_{20}(PO)_{70}(EO)_{20} (Pluronic P123, Aldrich) was dissolved in aqueous solution of HCl (500 ml), and it was stirred for 4 h. 8.5 g of Sucrose (TCI) and 7.5 ml of H_{2}SO_{4} solution were then added into the solution with vigorous stirring for 1 h. 36 ml of TEOS (tetraethyl orthosilicate, Aldrich) was additionally added into the mixed solution with constant stirring for 24 h. The solution was kept at 100 °C for 20 h under static condition. The mixture was dried at 100 °C for 50 h, and it was carbonized at 800 °C for 4 h under a nitrogen flow (100 ml/min) at a heating rate of 5 °C/min. Silica template was removed from resulting solid mixture by treating with 50 wt% HF solution. After washing, filtering, and drying the resultant, ordered mesoporous carbon (OMC) was obtained.

Sulfonated ordered mesoporous carbon supports were prepared by a covalent attachment of sulfonating agent (sulfonic acid-containing aryl radical) according to the similar methods reported in the literature [12]. Sulfonating agent (4-benzenediazonium sulfonate) was synthesized by diazotitbation of p-sulfanilic acid. 1 g of OMC was added into the mixture of de-ionized water (100 ml) and ethanol (100 ml). The mixture was stirred for
30 min at 5 °C. A known amount of prepared 4-diazoniumbenzene sulfonate and 100 ml of hypophosphorous acid (H₃PO₂, DAEJUNG) were added into the mixture under vigorous stirring. After stirring the mixture for 30 min, additional 100 ml of hypophosphorous acid was added under stirring for 1 h at 5 °C. After filtering the resulting product, it was washed with de-ionized water and ethanol repeatedly, and finally, it was dried at 60 °C. The obtained sulfonated ordered mesoporous carbon supports were denoted as OMC-S-X (X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25), where X represented the weight ratio of 4-benzenediazonium sulfonate with respect to OMC.

For impregnation of palladium onto sulfonated carbon support, palladium chloride (PdCl₂, Sigma-Aldrich) was dissolved in acetone solution containing 0.1 M hydrochloric acid. Palladium loading was fixed to 2.5 wt% for all samples. The solution containing palladium precursor was then introduced onto OMC-S-X support by an incipient wetness impregnation method. After drying the impregnated sample at 60 °C, it was calcined at 300 °C for 4 h at a heating rate of 5 °C/min under a nitrogen flow (85 ml/min). The catalyst was reduced at 200 °C under the mixed flow of H₂ (2.5 ml/min) and N₂ (47.5 ml/min) for use in the reaction. The prepared catalysts were denoted as Pd/OMC-S-X (X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).
Fig. 2.1.4. Schematic procedures for the preparation of palladium catalysts supported on sulfonated ordered mesoporous carbon (Pd/OMC-S-X, X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).
2.2. Characterization

2.2.1. Textural properties

Textural properties of prepared catalysts were investigated by nitrogen adsorption-desorption measurements using a BET apparatus (Micromeritics, ASAP 2010). The Brunauer-Emmett-Teller (BET) equation was used to calculate surface area of the catalysts. Surface areas of the catalysts were calculated by the Brunauer-Emmett-Teller (BET) method. Before the measurements, the catalysts were degassed at 120 °C for 4 h by vacuum pump for removal of moisture and other adsorbed gases on the surface of samples.

2.2.2. Crystalline structure

X-ray diffraction (XRD) analyses were performed using D-MAX-2500-PC (Rigaku) diffractometer operated at 40 kV and 100 mA to examine crystalline characteristics of reduced catalysts. Diffraction data were collected under Cu-Kα radiation (λ= 1.514 Å) with a scan rate 10 °/min.

2.2.3. Metal dispersion

CO chemisorption experiments were performed using a BELCAT-B instrument (BEL Japan). 10 mg of calcined catalyst was reduced at 500 °C for 4 h with a heating rate of 5 °C/min, and then 5% CO/He mixed gas was
periodically injected at 100 °C. Metal surface area, metal dispersion, and average metal particle size were calculated from the amount of carbon monoxide adsorbed on the reduced catalyst by assuming that one carbon monoxide molecule occupies one surface metal atom.

### 2.2.4. Morphological features

Particle size distribution of the prepared nanoparticles and Pore structure and pore size of prepared catalysts were examined by transmission electron microscopy (TEM) analyses (JEM-3010, JEOL). The particle size of palladium nanoparticles was calculated on the basis of edge distance of particle in the TEM image by assuming that the shape of metal particle is cube.

### 2.2.5. Acid properties

NH$_3$-temperature-programmed desorption (TPD) experiments were conducted in order to measure acidity of the catalysts. For the TPD measurements, 20 mg of each catalyst sample was charged into a tubular reactor of TPD apparatus. Prior to the NH$_3$-TPD measurements, the catalyst was preheated at 200 °C for 1 h under a He flow (20 ml/min) to eliminate physisorbed organics. Ammonia (20 ml/min) was then pulse-introduced into the reactor every minute at room temperature in a stream of He (5 mL/min), until the acid site was saturated with ammonia. The catalyst was evacuated at 50 °C for 1 h to remove physisorbed ammonia. Furnace temperature was
increased from room temperature to 600 °C at a heating rate of 5 °C/min under a He flow (10 ml/min). Desorbed ammonia was detected using a GC-MSD (Agilent, MSD-6890N GC).

2.2.6. Chemical state studies

Temperature-programmed reduction (TPR) analyses of the catalysts were performed in a flow reactor system equipped with a quartz reactor. 50 mg of the catalyst was pretreated with N₂ flow (50 ml/min) at 200 °C for 1 h, and TPR profiles were subsequently obtained using a thermal conductivity detector (TCD) at temperatures ranging from room temperature to 500 °C with a heating rate of 5 °C/min under 5% H₂/N₂ flow (50 ml/min).

Chemical state of palladium nanoparticles was investigated by FT-IR analysis (Nicolet, Nicolet 6700). Thermogravimetric analyses (TGA) were conducted to examine the thermal stability of palladium nanoparticles at a heating rate of 10 °C/min under N₂ flow (TA instrument, A600).
2.3. Direct synthesis of hydrogen peroxide

Direct synthesis of hydrogen peroxide from hydrogen and oxygen was performed in an autoclave reactor as shown in Fig. 2.3. 80 ml of methanol (Sigma-Aldrich), halide additive (for all samples) and acid additive (only for some samples) were charged into the reactor. Sodium bromide (NaBr, Sigma-Aldrich) was used as halide and sulfuric acid (1M H₂SO₄, Samchun chemicals) was used as acid additive. Concentrations of additives were fixed at 100 ppm for sodium bromide and 1000 ppm for sulfuric acid. Known amount of each catalyst was then added into the reactor. H₂/N₂ (25 mol% H₂) gas and O₂/N₂ (50 mol% O₂) gas were bubbled through the reaction medium in the reactor. Total flow rate of reactant gases was maintained at 44 ml/min, and H₂ concentration was fixed at 4 mol%. The reaction was carried out at 28 °C and 10 bar for 2 h under vigorous stirring (1000 rpm). The amount of unreacted hydrogen was measured using a gas chromatograph (Younglin, ACME 6000) equipped with a thermal conductivity detector. The concentration of hydrogen peroxide was determined by iodometric titration method [48]. Conversion of hydrogen, selectivity for hydrogen peroxide, and yield for hydrogen peroxide were calculated according to the following equations.

\[
\text{Conversion of hydrogen (\%)} = \frac{\text{moles of hydrogen reacted}}{\text{moles of hydrogen supplied}} \times 100
\]  

(2.1)
Selectivity for hydrogen peroxide (%) 

\[
= \frac{\text{moles of hydrogen peroxide formed}}{\text{moles of hydrogen reacted}} \times 100 \tag{2.2}
\]

Yield for hydrogen peroxide (%) 

\[
= (\text{Conversion of hydrogen}) \times (\text{Selectivity for hydrogen peroxide}) /100 \tag{2.3}
\]
Fig. 2.3. Reaction apparatus for direct synthesis of hydrogen peroxide.
Table 2.3

Reaction conditions for direct synthesis of hydrogen peroxide.

<table>
<thead>
<tr>
<th>Operation variable</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>28 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>10 bar</td>
</tr>
<tr>
<td>Agitation speed</td>
<td>1000 rpm</td>
</tr>
<tr>
<td>Solvent</td>
<td>80 ml methanol</td>
</tr>
<tr>
<td>Reactant gas feed</td>
<td>H₂/O₂/N₂ = 4/42/54</td>
</tr>
<tr>
<td>Catalyst</td>
<td>0.1 g (nanoparticle catalysts)</td>
</tr>
<tr>
<td></td>
<td>0.2 g (other catalysts)</td>
</tr>
</tbody>
</table>
Chapter 3. Results and Discussion

3.1. Size-controlled palladium nanoparticle catalysts

3.1.1. Morphology of palladium nanoparticles

Pd nanocubes were successfully prepared using different types of stabilizing agents; PVP and TTAB. Fig. 3.1.1 shows the HR-TEM images of Pd nanocubes prepared using PVP. To obtain nanocubes with different particle size, various ratios of halide ion surfactant (NaBr) with respect to reducing agent (ascorbic acid) were tested. It was observed that the ratio of halide ion surfactant with respect to reducing agent strongly affected the size of nanoparticles. The size of Pd nanocube increased with increasing ratio of halide ion surfactant with respect to reducing agent. As shown in Fig. 3.1.1 (a)-(c), average particle sizes of PVP-stabilized Pd nanocubes were 12, 15, and 18 nm, respectively (PVP-12PC, PVP-15PC, and PVP-18PC). The ratios of halide ion surfactant with respect to reducing agent used in the preparation of nanocubes were 3.7, 7.4, and 14.7, respectively. When the ratio was less than 3.7 or more than 14.7, the cubic shape of Pd particles was not maintained. According to the literature, halide ions coordinate to Pd cations, forming ligand complexes [49]. As a result, Br⁻ ions impede the reduction of Pd precursor during the synthesis, resulting in the growth of Pd particles. Halide ions also serve as a shape-controlling agent through adsorption onto the {100}
surfaces of Pd [47]. The presence of Br⁻ ions promoted the formation of Pd nanocubes, as revealed in this work. Thus, the size of Pd nanocubes could be controlled by adjusting the ratio of halide ion/reducing agent.

Fig. 3.1.2 shows the HR-TEM images of Pd nanocubes prepared using TTAB. In the preparation of nanocubes with different particle size, various ratios of surfactant (TTAB) with respect to reducing agent were also examined. The size of Pd nanocube increased with increasing ratio of surfactant with respect to reducing agent. As shown in Fig. 3.1.2 (a)-(c), average particle sizes of TTAB-stabilized Pd nanocubes were 18, 26, and 33 nm, respectively (TTAB-18PC, TTAB-26PC, and TTAB-33PC). The ratios of surfactant with respect to reducing agent were 0.16, 1.56, and 15.6, respectively. It has been reported that alkylammonium halides interact with Pd precursors to form a metal-surfactant complex, stabilizing Pd with ammonium and Br⁻ ions [50]. Because concentration of two different ions can’t be controlled separately, some particles were aggregated. The cubic shape evolution and size variation of nanoparticles, however, could be achieved by adjusting the ratio of TTAB/reducing agent in this work.
Fig. 3.1.1. HR-TEM images of Pd nanocubes with different size prepared using PVP as a stabilizer: (a) PVP-12PC, (b) PVP-15PC, and (c) PVP-18PC.
Fig. 3.1.2. HR-TEM images of Pd nanocubes with different size prepared using TTAB as a stabilizer:

(a) TTAB-18PC, (b) TTAB-25PC, and (c) TTAB-33PC.
3.1.2. Catalytic performance of palladium nanoparticle catalysts supported on alumina

Catalytic performance of impregnated catalysts in the direct synthesis of hydrogen peroxide was tested in the presence of acid (H$_2$SO$_4$) and halide (NaBr) promoters. Fig. 3.1.3 shows the catalytic activities of PVP-XPC/Al$_2$O$_3$ (X=12, 15, 18) and TTAB-XPC/Al$_2$O$_3$ (X=18, 25, 33) catalysts in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. In both series of catalysts, conversion of hydrogen increased with decreasing size of Pd nanocubes. As the size of nanocube decreases, the fraction of atoms on {100} surface in the cube increases. Therefore, smaller Pd nanocubes provide more active sites for reactants, resulting in the increase of hydrogen conversion. Selectivity for hydrogen peroxide also increased with decreasing size of Pd nanocubes, indicating that undesired side reactions were suppressed with smaller nanocubes. Selectivity for hydrogen peroxide depends on side reactions such as decomposition of hydrogen peroxide and combustion of hydrogen, and the side reactions are known to be promoted by O-O bond dissociation [16]. The dissociation of O-O bonds in oxygen and hydrogen peroxide molecules causes the formation of water, leading to the decrease in hydrogen peroxide selectivity. According to the literature, molecular oxygen is easily dissociated to atomic oxygen on the Pd {100} surface [51]. Because the fraction of {100} surface atoms increases, the dissociation of O-O bonds is possibly easier to arise, with decreasing the Pd particle size. Nevertheless, the side reactions were suppressed by the action of halide additive. Halide
additives are known to enhance the hydrogen peroxide selectivity by partially blocking adsorption sites of Pd surface and by modifying the electronic states of Pd [52]. It has also been reported that the presence of bromide additive prohibited the decrease of hydrogen peroxide selectivity, which was well consistent with the previous results [53].
Fig. 3.1.3. Catalytic performance of PVP-XPC/Al₂O₃ (X=12, 15, 18) and TTAB-XPC/Al₂O₃ (X=18, 25, 33) catalysts in the direct synthesis of hydrogen peroxide.
3.1.3. Effect of stabilizing agent on the catalytic performance of palladium nanoparticle catalysts

In order to examine the effect of stabilizing agent, catalytic performance of PVP- and TTAB-stabilized Pd nanocube catalysts with a similar particle size was compared. Fig. 3.1.4 shows the catalytic activities of PVP-18PC/Al₂O₃ and TTAB-18PC/Al₂O₃ catalysts in the direct synthesis of hydrogen peroxide. Hydrogen conversion and hydrogen peroxide selectivity of TTAB-18PC/Al₂O₃ were higher than those of PVP-18PC/Al₂O₃. Considering that the catalytic performance strongly depends on the particle size of Pd nanocubes prepared with the same stabilizing agent, it is quite interesting to see that two samples with a similar particle size show different catalytic activity. The above result implies that the catalytic activity in the direct synthesis of hydrogen peroxide is also influenced by the stabilizing agent.

To elucidate the different catalytic performance of PVP-18PC/Al₂O₃ and TTAB-18PC/Al₂O₃ catalysts, FT-IR spectroscopy measurements of Pd nanocubes were conducted. Fig. 3.1.5 shows the FT-IR spectra of pure PVP, PVP-18PC, pure TTAB, and TTAB-18PC. IR bands were assigned according to the literatures [29,54]. PVP-18PC sample exhibited the IR bands attributed to C=O and C-N (1290, 1490 and 1675 cm⁻¹) with quite strong peak intensity, while TTAB-18PC only showed the IR bands attributed to C-H (2840, 2870 and 2890 cm⁻¹) with weak intensity. This result indicates that chemical species containing C=O and C-N bonds from pyrrolidone remained on the surface of
Pd after the preparation of PVP-18PC nanocubes, whereas ammonium or Br⁻ from TTAB rarely remained on the surface of Pd after the preparation of TTAB-18PC nanocubes.

TGA analyses were carried out to examine the thermal stability of Pd nanocubes. Fig. 3.1.6 shows the TGA curves of PVP-18PC and TTAB-18PC. TGA results revealed that PVP-18PC was thermally decomposed via multiple steps (200~450 °C), indicating the presence of pyrrolidone species on the Pd surface. On the other hand, TTAB-18PC showed only a small amount of mass decrease under 200 °C, indicating that only a small C-H fraction was left. These results were in good agreement with the FT-IR results.

Considering the FT-IR and TGA results, the different catalytic performance of PVP-18PC/Al₂O₃ and TTAB-18PC/Al₂O₃ catalysts is likely due to the difference in remaining chemical species on the Pd surface. In case of PVP-18PC, strong chemical bonds such as C=O and C-N from pyrrolidone remained on the surface, inhibiting the access of reactants and promoters. On the other hand, only a small amount of alkyl species remained on the TTAB-18PC surface. As a consequence, adsorption of hydrogen and contact of promoters to Pd sites occurred more easily over TTAB-18PC than PVP-18PC, resulting in higher catalytic activity of TTAB-18PC/Al₂O₃ in the direct synthesis of hydrogen peroxide.
Fig. 3.1.4. Comparison of catalytic performance of PVP-18PC and TTAB-18PC.
Fig. 3.1.5. FT-IR spectra of (a) pure PVP and PVP-18PC, and (b) pure TTAB and TTAB-18PC.
Fig. 3.1.6. TGA curves for PVP-18PC and TTAB-18PC.
3.2. Palladium catalysts supported on heteropolyacid-containing ordered mesoporous carbon

3.2.1. Formation of palladium catalysts supported on ordered mesoporous carbon

Textural properties of the catalysts were examined by nitrogen adsorption-desorption measurements. Nitrogen adsorption-desorption isotherms of Pd/OMC-T catalysts (T = 8, 15, 25, 35, and 45 °C) are shown in Fig. 3.2.1. All the catalysts exhibited type-IV isotherm and hysteresis loop [55]. This indicates that the mesoporous pore structure of the catalysts was maintained even after the impregnation of palladium onto OMC. Fig. 3.2.2 shows the results of XRD analyses. XRD patterns of Pd/OMC-T catalysts showed typical peaks for graphitic carbon at 23.5° and 43.8°, and only a small peak of Pd(111) at 40° in the Pd/OMC-8, 15, 45 catalysts. This means that palladium species were finely dispersed on the surface of the catalysts through well-developed pore in the samples with high surface area (Pd/OMC-25,35). Whereas, crystal growth of palladium was observed in Pd/OMC-8,15,45 samples due to their decreased surface area. BET surface area of Pd/OMC-T catalysts (T = 8, 15, 25, 35, and 45 °C) are listed in Table 3.2.1. Surface area of the catalysts showed in a volcano-shaped trend with respect to temperature of OMC. Among the catalysts, Pd/OMC-25 catalyst exhibited the highest surface area. It is known that the behavior of surfactant micelle significantly affects the surface property of resulting support materials in the
surfactant-templating method [56]. The micelle size of P123 block copolymer might be changed by controlling the solution temperature, influencing the size and structure of silica-carbon precursor complexes. It is believed that the micelle size of P123 decreases with decreasing solution temperature to 25 °C, resulting in a decrease of ordered array size of OMC and an increase in the surface area. The low surface area of Pd/OMC-8 and 15 catalysts might be because an appropriate micelle structure was not formed at low temperature [57,58].
Fig. 3.2.1. Nitrogen adsorption-desorption isotherms of Pd/OMC-T catalysts (T = 8, 15, 25, 35, and 45 °C).
Table 3.2.1
Textural properties of Pd/OMC-T catalysts (T = 8, 15, 25, 35, and 45 °C).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)ᵃ</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/OMC-8</td>
<td>302</td>
<td>0.24</td>
<td>3.01</td>
</tr>
<tr>
<td>Pd/OMC-15</td>
<td>957</td>
<td>1.19</td>
<td>3.99</td>
</tr>
<tr>
<td>Pd/OMC-25</td>
<td>1549</td>
<td>1.89</td>
<td>3.85</td>
</tr>
<tr>
<td>Pd/OMC-35</td>
<td>1083</td>
<td>1.47</td>
<td>4.47</td>
</tr>
<tr>
<td>Pd/OMC-45</td>
<td>624</td>
<td>0.81</td>
<td>3.76</td>
</tr>
</tbody>
</table>

ᵃ Calculated by BET equation  
ᵇ Total pore volume at P/P₀ = 0.99  
ᶜ Average pore diameter
Fig. 3.2.2. XRD patterns of Pd/OMC-T catalysts (T = 8, 15, 25, 35, and 45 °C).
In order to confirm the pore size and structure of the catalysts, TEM analyses were conducted. Fig. 3.2.3 shows the HR-TEM images of Pd/OMC-T catalysts (T = 8, 15, 25, 35, and 45 °C). Ordered arrays of carbon supports with a pore size of 5~10 nm were observed in the Pd/OMC-15, 25, 35, and 45 catalysts, while Pd/OMC-8 exhibited a non-ordered carbon structure. This results were in accordance with the results of nitrogen adsorption-desorption measurements. Thus, surface area and pore size of the catalysts could be controlled by changing preparation temperature of OMC as attempted in this work.
Fig. 3.2.3. HR-TEM images of Pd/OMC-T catalysts

(T = 8, 15, 25, 35, and 45 °C).
3.2.2. Catalytic activity of palladium catalysts supported on ordered mesoporous carbon

Catalytic activity of Pd/OMC-T catalysts (T = 8, 15, 25, 35, and 45 °C) in the direct synthesis of hydrogen peroxide performed in the presence of NaBr and H₂SO₄ at 28 °C for 6 h is presented in Fig. 3.2.4. Conversion of hydrogen, selectivity for hydrogen peroxide, and yield for hydrogen peroxide showed volcano-shaped trends with respect to preparation temperature of OMC supports. Among the catalysts, Pd/OMC-25 catalyst showed the highest conversion and selectivity, leading to the largest yield for hydrogen peroxide.

In order to elucidate the relationship between catalyst property and catalytic performance, palladium dispersion and palladium surface area of the catalysts were measured by CO chemisorption technique. CO chemisorption results for Pd/OMC-T catalysts (T = 8, 15, 25, 35, and 45 °C) are listed in Table 3.2.2. It was found that palladium dispersion and palladium surface area increased with increasing BET surface area of the catalysts. It is well known that high surface area of supporting material facilitates dispersion of active metal, resulting in an increase of metal surface area [59]. The catalyst with high metal surface provides more adsorption sites for reactants, enhancing the conversion value. Therefore, it is inferred that the increase of surface area caused well-dispersed palladium onto OMC support, leading to an increase of conversion of hydrogen.
Fig. 3.2.4. Catalytic performance of Pd/OMC-T catalysts

(T = 8, 15, 25, 35, and 45 °C).
Table 3.2.2

CO chemisorption results of Pd/OMC-T catalysts
(T = 8, 15, 25, 35, and 45 °C).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Palladium dispersion (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Palladium surface area (m&lt;sup&gt;2&lt;/sup&gt;/g)&lt;sup&gt;a&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td>Pd/OMC-45</td>
<td>9.9</td>
<td>44.2</td>
</tr>
<tr>
<td>Pd/OMC-35</td>
<td>19.5</td>
<td>85.8</td>
</tr>
<tr>
<td>Pd/OMC-25</td>
<td>25.9</td>
<td>115.3</td>
</tr>
<tr>
<td>Pd/OMC-15</td>
<td>17.3</td>
<td>76.6</td>
</tr>
<tr>
<td>Pd/OMC-8</td>
<td>6.9</td>
<td>30.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from CO chemisorption measurement by assuming a stoichiometry factor of CO/metal<sub>atom</sub> = 1
3.2.3. Formation of palladium catalysts supported on heteropolyacid-containing ordered mesoporous carbon

Fig. 3.2.5 shows the results of nitrogen adsorption-desorption measurements of Pd/OMC-XHPA catalysts (X = 5, 10, 20, 30, and 40 wt%). Nitrogen adsorption-desorption isotherms of Pd/OMC-XHPA catalysts showed type-IV isotherm with hysteresis loop, which were similar to those of Pd/OMC-25. This result supports that pore structure of carbon was maintained even after the impregnation of heteropolyacid (Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$) and palladium on the surface of OMC. BET surface area of Pd/OMC-XHPA catalysts are summarized in Table 3.2.3. Surface areas of Pd/OMC-XHPA catalysts decreased with increasing HPA content. This was attributed to the partial blockage of OMC pores by heteropolyacid aggregates.

Fig. 3.2.6 shows the XRD patterns of Pd/OMC-XHPA catalysts (X = 5, 10, 20, 30, and 40 wt%). The diffraction peaks for heteropolyacid were not observed in the Pd/OMC-XHPA catalysts (X = 5, 10, and 20 wt%) because of fine dispersion of HPA onto OMC. On the other hand, distinct diffraction peaks for HPA were shown in the Pd/OMC-XHPA catalysts (X = 30 and 40 wt%), and XRD peak intensity increased with increasing HPA content. However, any peaks for palladium were not detected due to its fine dispersion onto OMC-XHPA supports.

Fig. 3.2.7 shows the HR-TEM images of Pd/OMC-XHPA catalysts (X = 5, 10, 20, 30, and 40 wt%). Carbon morphology and pore structure of the catalysts were similar to those of the sample without HPA (Pd/OMC-25),
indicating the catalysts retained an ordered porous structure even after HPA and palladium loading on OMC. It is noteworthy that Pd/OMC-XHPA (X = 10, and 20 wt%) exhibited only ordered array of carbon supports with no aggregation of HPA, while significant aggregate of HPA were observed in Pd/OMC-XHPA catalysts (X = 30 and 40 wt%). This result is well consistent with the results of XRD and nitrogen adsorption-desorption analyses.
Fig. 3.2.5. Nitrogen adsorption-desorption isotherms of Pd/OMC-XHPA catalysts ($X = 5, 10, 20, 30$, and $40$ wt%).
Table 3.2.3

Textural properties of Pd/OMC-XHPA catalysts

(X = 5, 10, 20, 30, and 40 wt%).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)ᵃ</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/OMC-5HPA</td>
<td>1128</td>
<td>1.40</td>
<td>3.98</td>
</tr>
<tr>
<td>Pd/OMC-10HPA</td>
<td>1101</td>
<td>1.36</td>
<td>3.98</td>
</tr>
<tr>
<td>Pd/OMC-20HPA</td>
<td>1003</td>
<td>1.13</td>
<td>4.02</td>
</tr>
<tr>
<td>Pd/OMC-30HPA</td>
<td>949</td>
<td>1.02</td>
<td>3.72</td>
</tr>
<tr>
<td>Pd/OMC-40HPA</td>
<td>743</td>
<td>0.94</td>
<td>4.01</td>
</tr>
</tbody>
</table>

ᵃ Calculated by BET equation
ᵇ Total pore volume at P/P₀ = 0.99
ᶜ Average pore diameter
Fig. 3.2.6. XRD patterns of Pd/OMC-XHPA catalysts

(X = 5, 10, 20, 30, and 40 wt%).
Fig. 3.2.7. TEM images of Pd/OMC-XHPA catalysts

(X = 5, 10, 20, 30, and 40 wt%).
3.2.4. Acid property of palladium catalysts supported on heteropolyacid-containing ordered mesoporous carbon

NH$_3$-TPD experiments were performed over Pd/OMC-XHPA catalysts (X = 5, 10, 20, 30, and 40 wt%) in order to measure acidity of the catalysts. Fig. 3.2.8 shows the NH$_3$-TPD profiles of Pd/OMC-XHPA catalysts. Acidity of Pd/OMC-XHPA catalysts was measured from NH$_3$-TPD peak area of the catalyst. Cs ion-exchanged heteropolyacid is known to have Brönsted acid sites [60]. Consequently, acid amount of Brönsted acid sites can be obtained from NH$_3$-TPD peak area. Acidity of Pd/OMC-XHPA catalysts is listed in Table 3.2.4. It is quite interesting to note that acidity of the catalysts showed the volcano-shaped trend with respect to HPA content. Among the catalysts, Pd/OMC-20HPA catalyst exhibited the largest acidity. It has been reported that pore blockage by HPA aggregation causes a decrease in acidity even at high HPA loading [61]. It was found that the aggregation abruptly occurred at a HPA content higher than 20 wt%, as evidenced by TEM and nitrogen adsorption-desorption analyses in this work. Accordingly, it can be inferred that the decreased acidity of Pd/OMC-XHPA (X = 30 and 40 wt%) was due to the limited adsorption site for ammonia.
Fig. 3.2.8. NH$_3$-TPD profiles of Pd/OMC-XHPA catalysts  
(X = 5, 10, 20, 30, and 40 wt%).
Table 3.2.4

Acidity of Pd/OMC-XHPA catalysts (X = 5, 10, 20, 30, and 40 wt%).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acidity (μmol-NH$_3$/g-catalyst)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/OMC-5HPA</td>
<td>45</td>
</tr>
<tr>
<td>Pd/OMC-10HPA</td>
<td>82</td>
</tr>
<tr>
<td>Pd/OMC-20HPA</td>
<td>161</td>
</tr>
<tr>
<td>Pd/OMC-30HPA</td>
<td>138</td>
</tr>
<tr>
<td>Pd/OMC-40HPA</td>
<td>96</td>
</tr>
</tbody>
</table>

$^a$ Measured by NH$_3$-TPD analyses
3.2.5. Catalytic activity of palladium catalysts supported on heteropolyacid-containing ordered mesoporous carbon

Reaction test for direct synthesis of hydrogen peroxide was performed only in the presence of NaBr (no acid additive) at 28 °C for 6 h with Pd/OMC-XHPA catalysts (X = 5, 10, 20, 30, and 40 wt%). Fig. 3.2.9 shows the catalytic performance of Pd/OMC-XHPA catalysts in the direct synthesis of hydrogen peroxide from hydrogen and oxygen in the absence of acid promoter. Conversion of hydrogen exhibited no great difference (higher than 90%) over all Pd/OMC-XHPA catalysts, while selectivity for hydrogen peroxide showed volcano-shaped trend with respect to HPA content. As a consequence, yield for hydrogen peroxide also showed a volcano-shaped trend with respect to HPA content. Among the catalysts tested, Pd/OMC-20HPA presented the highest selectivity (34.1 %) and yield (32.2 %) for hydrogen peroxide. It is believed that the difference in catalytic performance of Pd/OMC-XHPA catalysts is likely to result from the amount of active HPA.
Fig. 3.2.9. Catalytic performance of Pd/OMC-XHPA catalysts

\(X = 5, 10, 20, 30, \text{ and } 40 \text{ wt\%} \).
3.2.6. Correlation between acid property and catalytic activity of palladium catalysts supported on heteropolyacid-containing ordered mesoporous carbon

According to the results of characterization and the catalytic performance of Pd/OMC-XHPA catalysts, yield for hydrogen peroxide is intimately related to the acidity of the catalysts, as shown in Fig. 3.2.10. Among the Pd/OMC-XHPA catalysts, the highest yield for hydrogen peroxide was achieved over Pd/OMC-20HPA with the largest acidity. It has been reported that surface acidity of the catalyst plays an important role for improving the catalytic performance in the direct synthesis of hydrogen peroxide by preventing decomposition of hydrogen peroxide [62]. Therefore, it is concluded that the improved acidity of the catalyst led to the enhancement in the yield of hydrogen peroxide.
Fig. 3.2.10. A correlation between yield for hydrogen peroxide over Pd/OMC-XHPA catalysts (X = 5, 10, 20, 30, and 40 wt%) and acidity of the catalysts.
3.3. Palladium catalysts supported on sulfonated ordered mesoporous carbon

3.3.1. Formation of palladium catalysts supported on sulfonated ordered mesoporous carbon

Textural properties of Pd/OMC-S-X (X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25) catalysts were examined by nitrogen adsorption-desorption measurements as shown in Fig. 3.3.1. All the catalysts exhibited type-IV isotherm with H1-type hysteresis loop, indicating successful formation of cylindrical mesopores. BET surface areas and pore volumes of Pd/OMC-S-X catalysts are listed in Table 3.3.1. All the catalysts showed high surface area (>700 m²/g) and large pore volume (>0.8 cm³/g), indicating that the mesoporous structure of carbon support was maintained even after functionalization with sulfonating agent (4-benzenediazonium sulfonate). It was found that surface area and pore volume of the catalysts decreased with increasing the ratio of sulfonating agent in the catalysts. It is believed that sulfonating agent was attached onto the surface of OMC, resulting in gradual decrease of pore volume and surface area with increasing the ratio of sulfonating agent.

Crystalline structures of Pd/OMC-S-X catalysts were investigated by XRD analyses. No diffraction peaks for sulfur- or palladium-related species were detected in all the catalysts as shown in Fig. 3.3.2. This indicates that functionalization of OMC with sulfonic acid-containing radical led to no
formation of particular crystalline phase and palladium particles were finely dispersed on the catalyst surface. Fig. 3.3.3 shows the HR-TEM images of Pd/OMC-S-X catalysts. The images show that ordered arrays of mesoporous carbon was maintained in the samples treated with low ratio of sulfonating agent. However, non-ordered structure was partially observed over the ordered arrays in the catalysts treated with high ratio of sulfonating agent. This indicates that formation of non-ordered structure occurred on OMC support when excessive sulfonating agent was introduced. This result was well consistent with the gradual decrease of surface area of the catalysts with increasing the ratio of sulfonating agent (Table 3.3.1).
Fig. 3.3.1. Nitrogen adsorption-desorption isotherms of Pd/OMC-S-X catalysts (X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).
Table 3.3.1

Textural property of Pd/OMC-S-X catalysts
(X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g) ¹</th>
<th>Pore volume (cm³/g) ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/OMC-S-0.025</td>
<td>1076</td>
<td>1.46</td>
</tr>
<tr>
<td>Pd/OMC-S-0.05</td>
<td>1029</td>
<td>1.32</td>
</tr>
<tr>
<td>Pd/OMC-S-0.125</td>
<td>999</td>
<td>1.21</td>
</tr>
<tr>
<td>Pd/OMC-S-0.15</td>
<td>990</td>
<td>1.26</td>
</tr>
<tr>
<td>Pd/OMC-S-0.175</td>
<td>810</td>
<td>0.96</td>
</tr>
<tr>
<td>Pd/OMC-S-0.25</td>
<td>751</td>
<td>0.88</td>
</tr>
</tbody>
</table>

¹ Calculated by the BET equation
² Total pore volume at P/P₀ = 0.99
Fig. 3.3.2. XRD patterns of Pd/OMC-S-X catalysts
(X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).
Fig. 3.3. TEM images of Pd/OMC-S-X catalysts

(X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).
3.3.2. Acid property of palladium catalysts supported on sulfonated ordered mesoporous carbon

In order to investigate acid property of the catalysts, NH$_3$-TPD experiments were conducted over Pd/OMC-S-X catalysts. Fig. 3.3.4 shows NH$_3$-TPD profiles of Pd/OMC-S-X catalysts. Acid amount of the catalysts was calculated from the peak area of NH$_3$-TPD profiles as listed in Table 3.3.2. It was found that acidity of the catalysts increased with increasing the ratio of sulfonating agent. Sulfonated supporting materials are known to provide acid sites for adsorption of ammonia [63]. In this study, adsorption sites for ammonia (sulfonyl radicals or sulfonic acid functional groups) were formed on the surface of carbon support by the modification with sulfonating agent. Thus, the increase of acidity with increasing the ratio of sulfonating agent was due to the increased amount of sulfonyl radicals in the catalysts.
Fig. 3.3.4. NH$_3$-TPD profiles of Pd/OMC-S-X catalysts

(X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).
Table 3.3.2
Acidity of Pd/OMC-S-X catalysts
(X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acidity (μmol-NH₃ /g-catalyst)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/OMC-S-0.025</td>
<td>6</td>
</tr>
<tr>
<td>Pd/OMC-S-0.05</td>
<td>13</td>
</tr>
<tr>
<td>Pd/OMC-S-0.125</td>
<td>141</td>
</tr>
<tr>
<td>Pd/OMC-S-0.15</td>
<td>147</td>
</tr>
<tr>
<td>Pd/OMC-S-0.175</td>
<td>174</td>
</tr>
<tr>
<td>Pd/OMC-S-0.25</td>
<td>219</td>
</tr>
</tbody>
</table>

ᵃ Calculated from peak area of NH₃-TPD profile
3.3.3. Reduction behavior of palladium catalysts supported on sulfonated ordered mesoporous carbon

TPR analyses for Pd/OMC-S-X catalysts (X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25) were performed to measure reducibility of the catalysts. Fig. 3.3.5 shows the TPR spectra for calcined Pd/OMC-S-X catalysts. It was shown that Pd/OMC-S-X catalysts exhibited asymmetric reduction peaks below 200 °C, which are attributed to the reduction of palladium species [64]. The reducing temperatures of calcined Pd/OMC-S/X catalysts are summarized in Table 3.3.3. It was found that reducibility of the catalysts varied with increasing the ratio of sulfonating agent. The reduction temperature increased in the order of Pd/OMC-S-0.25 < Pd/OMC-S-0.175 < Pd/OMC-S-0.15 < Pd/OMC-S-0.025 < Pd/OMC-S-0.05 < Pd/OMC-S-0.125. It should be noted that the reduction temperature of catalysts showed a volcano-shaped trend with respect to the ratio of sulfonating agent. Sulfonic acid-containing functional groups, neighboring palladium atoms, strengthen the oxidizing character of palladium, because these functional groups withdraw electrons from palladium atoms [65]. When the content of sulfonic acid-containing group exceeds certain value, however, palladium sulfate phase becomes dominant due to excessive amount of sulfur [66]. The electrophilic character of the catalyst then decreases due to strong interaction between palladium and sulfur, resulting in broad TPR profile of the catalysts.
Fig. 3.3.5. TPR profiles of calcined Pd/OMC-S-X catalysts

\(X = 0.025, 0.05, 0.125, 0.15, 0.175, \text{ and } 0.25\).
Table 3.3.3

Reduction temperature of calcined Pd/OMC-S-X catalysts
(X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reducing temperature (°C)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/OMC-S-0.025</td>
<td>166.5</td>
</tr>
<tr>
<td>Pd/OMC-S-0.05</td>
<td>169.7</td>
</tr>
<tr>
<td>Pd/OMC-S-0.125</td>
<td>172.2</td>
</tr>
<tr>
<td>Pd/OMC-S-0.15</td>
<td>162.3</td>
</tr>
<tr>
<td>Pd/OMC-S-0.175</td>
<td>159.5</td>
</tr>
<tr>
<td>Pd/OMC-S-0.25</td>
<td>154.9</td>
</tr>
</tbody>
</table>

\(^a\) Obtained from peak point of reduction curve in Fig. 3.3.5
3.3.4. Catalytic performance of palladium catalysts supported on sulfonated ordered mesoporous carbon

Fig. 3.3.6 shows the catalytic performance of Pd/OMC-S-X catalysts (X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25) in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. It was found that Pd/OMC-S-X catalysts showed a considerably high activity in the absence of acid additive, indicating that sulfonated carbon support served as an acidic promoter in this reaction. It was observed that conversion of hydrogen monotonically decreased with increasing the ratio of sulfonating agent. It is believed that the increased acidity of the catalyst treated with high ratio of sulfonating agent induced strong interaction between palladium and sulfonated support and restricted access of reactants to palladium, causing decrement of hydrogen conversion. On the other hand, selectivity for hydrogen peroxide increased in the order of Pd/OMC-S-0.25 < Pd/OMC-S-0.175 < Pd/OMC-S-0.15 < Pd/OMC-S-0.025 < Pd/OMC-S-0.05 < Pd/OMC-S-0.125, which shows a volcano-shaped trend with respect to the ratio of sulfonating agent.
Fig. 3.3.6. Catalytic performance of Pd/OMC-S-X catalysts

\[(X = 0.025, 0.05, 0.125, 0.15, 0.175, \text{ and } 0.25).\]
3.3.5. Correlation between TPR result and catalytic activity of palladium catalysts supported on sulfonated ordered mesoporous carbon

The variation trend of catalytic performance is in good agreement with the trend of reduction temperature of the Pd/OMC-S-X catalysts. In the direct synthesis of hydrogen peroxide, electron transfer occurs from active palladium to adsorbed oxygen when oxygen molecule is adsorbed on the catalyst surface. Throughout the whole reaction, non-dissociative adsorption of oxygen molecule and desorption of hydro-peroxy species are required for selective formation of hydrogen peroxide [67]. It has been reported that oxidation state of catalyst plays an important role for selective formation of hydrogen peroxide in the direct synthesis from hydrogen and oxygen [68]. Fig. 3.3.7 shows the correlation between selectivity for hydrogen peroxide and reduction temperature of the Pd/OMC-S-X catalysts. It is noticeable that selectivity for hydrogen peroxide increased with increasing reduction temperature of the catalysts. As mentioned above, favorable catalytic reaction can be induced by reducing dissociation of molecular oxygen on catalyst surface. This implies that the suppressed movement of electron from palladium to adsorbed oxygen molecule, which was caused by the increased oxidizing character of the catalyst, enhances selectivity for hydrogen peroxide. Therefore, it is concluded that the enhanced selectivity for hydrogen peroxide over Pd/OMC-S-0.125 catalyst was due to the highest reduction temperature resulted from the introduction of sulfonating agent.
Fig. 3.3.7. Correlation between the reduction temperature and catalytic selectivity of Pd/OMC-S-X catalysts

(X = 0.025, 0.05, 0.125, 0.15, 0.175, and 0.25).
Chapter 4. Conclusions

Palladium catalysts were prepared in various forms such as size-controlled nanoparticles, supported catalysts on acidic solid supports. Then, prepared catalysts were employed for the direct synthesis of hydrogen peroxide to elucidate the effect of catalyst properties on the catalytic performance in the direct synthesis of hydrogen peroxide. The effect of particle size, roles of promoting additives, and introduction of solid acid in catalyst were investigated.

Size-controlled palladium (Pd) nanocubes were prepared by colloidal methods in the presence of different surface-stabilizing agents, polyvinylpyrrolidone (PVP) and tetradecyltrimethylammonium bromide (TTAB). The Pd nanocubes supported on γ-Al₂O₃ were applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Conversion of hydrogen and selectivity for hydrogen peroxide increased with decreasing size of Pd nanocubes. The effect of stabilizing agent was also investigated by comparing the catalytic activity of Pd nanocubes prepared with different stabilizing agent. TTAB-stabilized Pd nanocubes showed better catalytic activity than PVP-stabilized Pd nanocubes. It was revealed that strong C=O and C-N chemical bonding species remained on the PVP-stabilized Pd nanocubes, while only a small amount of alkyl species remained on the TTAB-stabilized Pd nanocubes. This different catalytic activity of Pd nanocubes was due to the difference in remaining chemical species on the Pd surface between PVP- and TTAB-stabilized nanocubes.
A series of palladium catalysts supported on the ordered mesoporous carbon were prepared by surfactant-templating and incipient wetness impregnation method with a variation of precursor solution temperature during the synthesis of OMC. Prepared catalysts were applied to direct synthesis of hydrogen peroxide from hydrogen and oxygen in the presence of halide and acid additives (NaBr and H₂SO₄). The effect of synthesis temperature on the physicochemical properties and catalytic activities of catalysts in the direct synthesis of hydrogen peroxide was investigated. Conversion of hydrogen and yield for hydrogen peroxide over Pd/OMC-T catalysts showed volcano-shaped trend with respect of the precursor solution temperature. The catalytic performance was found to be closely related to palladium surface area and growth of the specific crystal phase.

In an attempt not to use the liquid acid additive, another series of palladium catalysts supported on the heteropolyacid-containing ordered mesoporous carbon was prepared by incipient wetness impregnation and ion-exchanging method with different HPA contents. Prepared catalysts were applied to direct synthesis of hydrogen peroxide in the absence of acid additive. Selectivity and yield for hydrogen peroxide showed volcano-shaped curve with increasing the HPA content. The effect of different HPA content on the physicochemical properties and surface acidity of the catalysts was investigated. The acidity of Pd/OMC-XHPA catalyst also showed volcano-shaped trend with increasing the HPA content. The superior catalytic
performance of Pd/OMC-20HPA catalyst was due to its high surface acidity. Therefore, it was concluded that the improved catalytic performance for direct synthesis of hydrogen peroxide was achieved by controlling surface area of carbon support and enhancing the surface acidity of catalyst.

A series of ordered mesoporous carbon (OMC) were sulfonated by a covalent attachment of sulfonic acid-containing aryl radical with a variation of sulfonating agent (4-benzenediazonium sulfonate)/OMC ratio. Palladium catalysts supported on OMC-S-X were prepared by an incipient wetness impregnation method. Pd/OMC-S-X catalysts were then employed for direct synthesis of hydrogen peroxide from hydrogen and oxygen in the absence of acid additive. The effect of sulfonating agent ratio on the physicochemical properties and catalytic activities was investigated. Catalytic activity in the direct synthesis of hydrogen peroxide over Pd/OMC-S-X showed a volcano-shaped trend with respect to the ratio of sulfonating agent. Reducibility of oxidized Pd in the Pd/OMC-S-X catalysts was closely related to the catalytic performance. It was revealed that selectivity for hydrogen peroxide increased with increasing reduction temperature of the catalyst, indicating that oxidation state of catalyst played a significant role in improving catalytic activity in this reaction. Among the catalysts tested, Pd/OMC-S-0.125 with the highest reduction temperature showed the highest selectivity for hydrogen peroxide.

In summary, palladium nanoparticles and palladium supported on acidic supports such as heteropolyacid-introduced and sulfonated ordered mesoporous carbon were prepared, and they were applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. It was concluded
that palladium catalysts supported solid acid-introduced mesoporous carbon can be valid alternative acid source in the absence of acid additive.
Bibliography

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[54] Y. Borodko, S.E. Habas, M. Koebel, P. Yang, H. Frei, and G.A. Somorjai,


초 록

과산화수소는 여타 상업용 산화제 대비 강한 산화력을 나타내며, 산화반응을 일으킨 뒤 발생하는 부산물이 물과 산소 뿐인 친환경적인 특성을 갖기 때문에, 다양한 산업 분야에서 사용되고 있다. 그 사용 분야는 제지, 섬유 산업에서 전자, 폐수처리 등 매우 넓은 범위에 걸쳐 있으며, 화학 합성 공정의 산화제로도 사용된다. 1950년대부터 현재까지 상업적으로 판매되는 과산화수소는 2-알킬안트라퀴논을 자동산화 시키는 공정을 통해 생산되고 있다. 하지만 이 공정은 다량의 환경 유해한 용매의 사용과, 분리/정제에 들어가는 비용적 측면으로 인해 한계에 부딪혀 있다. 따라서 기존 공정을 대체하기 위한 대안으로 수소와 산소로부터 과산화수소를 직접 합성하는 반응에 대한 관심이 증가하여 왔다.

과산화수소를 직접 합성하는 반응은 목표로 하는 과산화수소 합성 반응 외에 수소와 산소로부터 물이 생성되는 반응, 과산화수소의 분해 반응과 같은 부반응이 활발히 발생하여 과산화수소의 선택도가 제한적이라는 문제점이 있어 아직 상업화에 이르지 못하고 있다. 이를 개선하기 위해 다양한 연구가 진행되어 왔다. 귀금속이 이 반응의 활성질소로 작용하는 데 특이 항아들이 높은 활성을 보이며, 산 및 화로겐 점거가 과산화수소 선택도를 향상시키는데 효과적인 것으로 밝혀졌다. 하지만 산 점거제의 사용은 반응장치의 부식과 축배 내 활성 금속의 용해를 유발하므로
이에 대한 개선이 필요하다. 이를 위해 측면 내 고체산을 적용하여 산첨가제를 대체하는 방법이 연구되어 왔으나, 여전히 높은 선택도와 수율을 얻기 위해서는 산첨가제의 사용이 필요한 실정이다. 본 연구에서는 팔라듐 나노입자를 제조하여 입자크기에 따른 반응성의 관계를 살펴보고, 산첨가제의 사용 없이 높은 과산화수소 선택도를 얻기 위하여 고체산이 도입된 담체를 제조한 후 팔라듐을 담지한 측면으로 과산화수소 직접 합성 반응을 진행하여 그에 따른 효과를 살펴 보았다.

두개의 다른 계면 안정화제를 사용하여 육면체 형상의 팔라듐 나노입자를 제조하고 이를 과산화수소 직접 합성 반응에 이용하였다. 계면 안정화제로 폴리비닐피로린(PVP)과 테트라데실트리메틸암모늄 브로마이드(TTAB)를 사용하였다. 안정화제의 두입 비율에 따라 크기가 다른 팔라듐 나노입자가 제조되는 것을 확인하였고, 제조된 나노입자들을 감마 알루미나 담체에 담지하여 과산화수소 직접 합성 반응에 적용하였다. 동일 안정화제를 사용한 경우, 팔라듐 입자의 크기가 감소할수록 수소 전환율이 증가하였으며, PVP를 사용한 경우보다 TTAB를 사용한 경우 팔라듐 나노입자 측면이 우수한 활성을 나타내었다. 적외선 분광분석과 열분해 분석을 통해, 안정화제에 따른 과산화수소 활성의 차이는 PVP로 제조된 팔라듐 입자 표면에 간류하는 C=O 와 C-N 과 같은 화학종에 따른 반응 원료의 제한적 환조에 의한 것임을 확인할 수 있었다.
계면활성 주형법으로 제조 시 용액의 온도를 조절하여 기공 크기와 표면 특성을 조절한 중형기공성 탄소 지지체를 제조하고, 거기에 Palladium을 담지하여 산점가체가 존재하는 조건에서 과산화수소 직접 합성 반응에 적용해 보았다. 제조 시 온도 조건에 따라 중형기공성 지지체의 비표면적이 화산형 곡선을 따라 변화하였고, 해당 촉매들 적용 시 과산화수소 수율 또한 화산형 곡선을 나타내었다. 지지체의 비표면적이 따른 Palladium의 분산도와 활성 면적이 반응 활성의 주요 인자라는 것을 알 수 있었다.

중형기공성 탄소 지지체에 헤테로폴리산을 도입한 산성 담체를 제조하고 거기에 Palladium을 담지한 촉매를 제조하고, 이를 산점가체 없는 조건에서 과산화수소 직접 합성 반응에 적용하였다. 이는 이온이 치환된 헤테로폴리산의 함량에 따라 촉매의 산특성이 증가하는 것을 확인하였다. 과산화수소 직접 합성 반응의 과산화수소 선택도 역시 동일한 경향성을 나타내었으며, 촉매의 표면 산성도가 증가할수록 과산화수소의 수율이 향상되는 것을 확인할 수 있었다. 이는 촉매 표면의 산특성이 과산화수소의 분해를 억제하는 역할을 했기 때문이라 할 수 있다.

중형기공성 탄소 지지체에 술폰화 반응을 통해 표면에 술폰기를 도입하여 술폰화된 탄소 지지체를 합성한 후 Palladium을 담지하고 과산화수소 직접 합성 반응에 적용하였다. 술폰화를 위해 사용한 술폰화제의 양에 따라 촉매의 산특성이 증가하는 경향을 보였으나, 과량의 술폰화제 사용에 따른 중형기공성 탄소의
비표면적 감소도 수반됨을 확인하였다. TPR 분석을 통해 수소화제의 양에 따라 촉매의 환원온도가 화산형 곡선을 따라 변화하였으며, 해당 촉매들의 과산화수소 직접 합성 수율 또한 화산형 곡선을 나타내는 것을 확인하였다. 이를 통해 촉매의 산화 상태가 과산화수소 직접 합성 반응의 수율에 중요한 역할을 하는 것을 알 수 있었다. 따라서 슬픈기의 도입에 따라 촉매에 산특성이 부여됨과 동시에 촉매의 전자적 특성이 변화되었고, 그것이 촉매의 산화-환원 특성에 영향을 끼쳐, 과산화수소의 부반응을 억제하는 주요 인자가 되었다고 할 수 있다.

본 연구에서는 Palladium 나노입자 촉매 및 산특성이 도입된 지지체에 담지된 Palladium 기반의 촉매를 제조하고, 과산화수소의 직접 합성 반응에 적용하였다. 제조된 촉매의 특성과 과산화수소 직접 합성 반응 수율과의 연관성을 설명하기 위해 질소 흡탈착 분석, XRD, TEM, FT-IR, TPR, NH₃-TPD 등의 다양한 분석을 실시하였고, 그 결과 Palladium 입자의 분산도와 촉매의 산특성, 그리고 전자적 상태가 과산화수소 직접 합성 반응의 수율에 중요한 역할을 할 수 확인할 수 있었다.

주요어: 과산화수소, 수소, 산소, Palladium 촉매, 중형기공성 탄소, 산성 지지체

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List of publications

International papers published (First author)


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Conferences

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Domestic conferences (First author)


Domestic conferences (Co-author)


6. 이어진, 이종원, 서영종, 이종원, 노영수, 이민재, 이종협, 송인규, “침전법으로 제조된 지르코늄 옥사이드에 담지된 은 촉매 상에서의
