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# Direct synthesis of hydrogen peroxide from hydrogen and oxygen over palladium catalyst supported on heteropolyacid-containing ordered mesoporous carbon

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## ABSTRACT

A series of palladium catalysts supported on ordered mesoporous carbon (Pd/OMC-T) were prepared with a variation of preparation temperature ( $T=8, 15, 25, 35,$  and  $45^{\circ}\text{C}$ ) of ordered mesoporous carbon (OMC). Conversion of hydrogen and yield for hydrogen peroxide over Pd/OMC-T catalysts showed volcano-shaped trends with respect of preparation temperature in the presence of halide and acid additives. The catalytic performance was found to be closely related to the palladium surface area. With an attempt not to use acid additive, another series of palladium catalysts supported on heteropolyacid (HPA)-containing ordered mesoporous carbon (Pd/OMC-XHPA) were prepared with a variation of HPA content ( $X=5, 10, 20, 30,$  and  $40\text{ wt}\%$ ) using OMC-25 as a support. Selectivity and yield for hydrogen peroxide showed volcano-shaped trends with respect to HPA content. The superior catalytic performance of the catalyst at a certain HPA content (Pd/OMC-20HPA) was attributed to its high acidity caused by introduction of HPA into the pores of the catalyst.

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## 1. Introduction

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 [1]. Although hydrogen peroxide has been commercially produced by anthraquinone auto-oxidation process for several decades, this process has severe drawbacks such as 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 [2].

Noble metal catalysts supported on various metal oxides have been extensively studied to enhance the yield for hydrogen peroxide [3]. However, the catalytic performance is not sufficient for commercialization due to side reactions. The side reactions are thermodynamically favorable with low activation energy. For this reason, halide and acid additives have been used to suppress the side reactions [4–7]. However, simultaneous use of halide and acid additives leads to leaching of active metal and corrosion of reactor.

To overcome this problem, supporting materials with acidic property have been investigated. Because these side reactions initiate with the adsorption of peroxide species on the surface of catalyst, hydrophobic property of supporting material is advantageous.

Carbon is a promising material as a support due to its hydrophobicity. Carbon supports can be prepared by several methods such as surfactant-templating method and RF (resorcinol-formaldehyde) polymerization method. In particular, pore size and pore structure of carbon support can be controlled by selecting different surfactant or by changing preparation conditions. For the direct synthesis of hydrogen peroxide, mesoporous carbon or activated carbon has been used to support active metal and to prevent side reactions [8,9].

Heteropolyacid (HPA) is inorganic acid. It is known that acidity of HPA is stronger than that of other solid acids. Thus, HPA has been applied as a solid acid catalyst in various acid-catalyzed reactions [10,11]. Although HPA is highly soluble in polar solvents, it has been reported that insoluble HPA with high surface area can be prepared by ion exchange with large cations such as  $\text{Cs}^+$  or  $\text{NH}_4^+$  [12,13]. It has also been reported that acidity of insoluble HPA can be controlled by changing the content of exchanging cations [14].

In this work, a series of palladium catalysts supported on ordered mesoporous carbon (Pd/OMC-T) were prepared by surfactant-templating and incipient wetness impregnation meth-

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ods with a variation of preparation temperature ( $T = 8, 15, 25, 35,$  and  $45\text{ }^\circ\text{C}$ ) of ordered mesoporous carbon (OMC). The effect of preparation temperature on the physicochemical properties and catalytic activities of Pd/OMC-T catalysts in the direct synthesis of hydrogen peroxide was investigated in the presence of halide and acid additives. Another series of palladium catalysts supported on heteropolyacid (HPA)-containing ordered mesoporous carbon (Pd/OMC-XHPA) were also prepared by incipient wetness impregnation and ion exchange method with a variation of HPA content ( $X = 5, 10, 20, 30,$  and  $40\text{ wt}\%$ ) with an attempt not to use acid additive. The effect of HPA content on the acidity and catalytic performance of the catalysts in the direct synthesis of hydrogen peroxide was investigated.

## 2. Experimental

### 2.1. Preparation of Pd/OMC-T catalysts ( $T = 8, 15, 25, 35,$ and $45\text{ }^\circ\text{C}$ )

Ordered mesoporous carbon supports (denoted as OMC-T,  $T = 8, 15, 25, 35,$  and  $45\text{ }^\circ\text{C}$ ) were prepared by a surfactant-templating method using P123 and TEOS as templates according to the similar methods reported in the literature [15].  $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$  triblock copolymer (Pluronic P123, Sigma-Aldrich) was dissolved in HCl solution (450 ml) at different temperature (8, 15, 25, 35, and  $45\text{ }^\circ\text{C}$ ) with constant stirring for 4 h. Carbon precursor material (Sucrose, TCI) and  $\text{H}_2\text{SO}_4$  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  $100\text{ }^\circ\text{C}$  for 20 h under static condition. The mixture was dried at  $100\text{ }^\circ\text{C}$  for 48 h, and then it was carbonized at  $800\text{ }^\circ\text{C}$  for 4 h at a heating rate of  $5\text{ }^\circ\text{C}/\text{min}$  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  $45\text{ }^\circ\text{C}$ ) by an incipient wetness impregnation method. Palladium chloride ( $\text{PdCl}_2$ , 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  $80\text{ }^\circ\text{C}$ , it was calcined at  $300\text{ }^\circ\text{C}$  for 3 h under a nitrogen flow. The supported catalysts were then reduced at  $200\text{ }^\circ\text{C}$  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  $45\text{ }^\circ\text{C}$ ), where T represented the preparation temperature of ordered mesoporous carbon in Celsius.

### 2.2. Preparation of Pd/OMC-XHPA catalysts ( $X = 5, 10, 20, 30,$ and $40\text{ wt}\%$ )

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 ( $\text{CsCl}$ , Sigma-Aldrich), and the mixture was stirred for 12 h for ion exchange. The collected solid was dried overnight at  $80\text{ }^\circ\text{C}$  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  $300\text{ }^\circ\text{C}$  for 3 h under a nitrogen flow to obtain OMC-XHPA ( $X = 5, 10, 20, 30,$  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. The prepared catalysts were denoted as Pd/OMC-XHPA ( $X = 5, 10, 20, 30,$  and  $40\text{ wt}\%$ ), where X represented the HPA ( $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ) content in ordered mesoporous carbon.

### 2.3. Characterization

Nitrogen adsorption-desorption isotherms of the catalysts were measured using a BET apparatus (Micromeritics, ASAP 2010). The Brunauer-Emmett-Teller (BET) equation was used to calculate surface area of the catalysts. Palladium dispersion and palladium surface area of the catalysts were determined by CO chemisorption experiments (BEL Japan, BELCAT-B). Crystalline states of the catalysts were examined by X-ray diffraction (XRD) measurements. XRD patterns of the catalysts were obtained by a D-Max2500-PC (Rigaku) instrument using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.541\text{ \AA}$ ) operated at 50 kV and 100 mA. Morphologies of Pd/OMC-T ( $T = 8, 15, 25, 35,$  and  $45\text{ }^\circ\text{C}$ ) and Pd/OMC-XHPA ( $X = 5, 10, 20, 30,$  and  $40\text{ wt}\%$ ) were examined by high resolution transmission electron microscopy (HR-TEM, Jeol, JEM-3010) analyses.  $\text{NH}_3$ -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  $\text{NH}_3$ -TPD measurements, the catalyst was preheated at  $200\text{ }^\circ\text{C}$  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  $50\text{ }^\circ\text{C}$  for 1 h to remove physisorbed ammonia. Furnace temperature was increased from room temperature to  $600\text{ }^\circ\text{C}$  at a heating rate of  $5\text{ }^\circ\text{C}/\text{min}$  under a He flow (10 ml/min). Desorbed ammonia was detected using a GC-MSD (Agilent, MSD-6890N GC).

### 2.4. Direct synthesis of hydrogen peroxide

Direct synthesis of hydrogen peroxide from hydrogen and oxygen was performed in an autoclave reactor. 80 ml of methanol and 0.2 g of catalyst were filled in the reactor. Sodium bromide (NaBr) and sulfuric acid (1 M  $\text{H}_2\text{SO}_4$ , Samchun chemicals) were then added as a halide additive and an acid additive, respectively. 100 ppm of sodium bromide and 300 ppm of sulfuric acid were used for Pd/OMC-T catalysts, while 100 ppm of sodium bromide was only used for Pd/OMC-XHPA catalysts.  $\text{H}_2/\text{N}_2$  (25 mol%  $\text{H}_2$ ) gas and

**Table 1**  
Physicochemical properties of Pd/OMC-T catalysts ( $T = 8, 15, 25, 35,$  and  $45\text{ }^\circ\text{C}$ ).

Catalyst	Surface area ( $\text{m}^2/\text{g}$ ) <sup>a</sup>	Palladium dispersion (%) <sup>b</sup>	Palladium surface area ( $\text{m}^2/\text{g}$ ) <sup>b</sup>
Pd/OMC-45	624	9.9	44.2
Pd/OMC-35	1083	19.5	85.8
Pd/OMC-25	1549	25.9	115.3
Pd/OMC-15	957	17.3	76.6
Pd/OMC-8	302	6.9	30.6

<sup>a</sup> Calculated by the BET equation.

<sup>b</sup> Measured by CO chemisorption by assuming  $\text{CO}/\text{Pd}_{\text{atom}} = 1$ .

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