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Direct synthesis of hydrogen peroxide from hydrogen and oxygen over palladium catalyst supported on SO_3H-functionalized MCF silica: Effect of calcination temperature of mesostructured cellular foam silica

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Abstract−Palladium catalysts supported on SO_3H-functionalized MCF silica (Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950)) were prepared with a variation of calcination temperature (T, °C) of MCF silica. They were then applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Conversion of hydrogen, selectivity for hydrogen peroxide, and yield for hydrogen peroxide showed volcano-shaped curves with respect to calcination temperature of MCF silica. Yield for hydrogen peroxide increased with increasing acid density of Pd/SO_3H-MCF-T catalysts. Thus, acid density of Pd/SO_3H-MCF-T catalysts played an important role in determining the catalytic performance in the direct synthesis of hydrogen peroxide. Pd/SO_3H-MCF-T catalysts efficiently served as an acid source and as an active metal catalyst in the direct synthesis of hydrogen peroxide.

Key words: Hydrogen Peroxide, Palladium, SO_3H-functionalized MCF Silica, Acid Density

INTRODUCTION

Hydrogen peroxide (H_2O_2) has been widely used as a clean and strong oxidant in various chemical processes [1-4]. Currently, it is mostly produced through the anthraquinone auto-oxidation process [1,2]. However, this process has several drawbacks such as use of toxic compounds and requirement of many energy-intensive steps for separation and purification of hydrogen peroxide [1,2]. Therefore, direct synthesis of hydrogen peroxide from hydrogen and oxygen has attracted much attention as an economical and environmentally benign process [5-14].

In the direct synthesis of hydrogen peroxide from hydrogen and oxygen, several undesired reactions occur together with selective oxidation of hydrogen to hydrogen peroxide ($H_2+O_2\rightarrow H_2O_2$, $\Delta H^o_{298\,K}=-135.8$ kJ/mol, $\Delta G^o_{298\,K}=-120.4$ kJ/mol) [1]. These undesired reactions include formation of water ($H_2+0.5O_2\rightarrow H_2O$, $\Delta H^o_{298\,K}=-241.6$ kJ/mol, $\Delta G^o_{298\,K}=-237.2$ kJ/mol), hydrogenation of hydrogen peroxide ($H_2O_2+H_2\rightarrow 2H_2O$, $\Delta H^o_{298\,K}=-211.5$ kJ/mol, $\Delta G^o_{298\,K}=-354.0$ kJ/mol), and decomposition of hydrogen peroxide ($H_2O_2\rightarrow H_2O+0.5O_2$, $\Delta H^o_{298\,K}=-105.8$ kJ/mol, $\Delta G^o_{298\,K}=-116.8$ kJ/mol) [1]. All these reactions are thermodynamically favorable and highly exothermic. In particular, water formation and hydrogenation of hydrogen peroxide are thermodynamically more favorable than selective oxidation of hydrogen to hydrogen peroxide. Consequently, selectivity for hydrogen peroxide in the direct synthesis of hydrogen peroxide is limited by these undesired reactions. Many attempts have been made to enhance the selectivity for hydrogen peroxide in the direct synthesis of hydrogen peroxide [6-14].

Acids such as phosphoric acid and sulfuric acid as well as halides such as bromide and chloride have been used as additives to increase the selectivity for hydrogen peroxide in the direct synthesis of hydrogen peroxide from hydrogen and oxygen [6-9]. Acids prevent the decomposition of hydrogen peroxide and halides inhibit the formation of water [1,2]. However, acids cause the dissolution of active metal component from the supported catalyst and accelerate the corrosion of reactor [1,2]. Therefore, solid acid supports have been employed for the direct synthesis of hydrogen peroxide as an alternate acid source [10-14].

Since SO_3H-functionalized mesoporous silicas have excellent acid property [15-20], they have been used as solid acid catalysts in acid-catalyzed reactions such as esterification and condensation [16-20]. In our previous work [14], palladium catalysts supported on SO_3H-functionalized mesoporous silicas were prepared using MCM-41, MCM-48, MSU-1, SBA-15, and mesostructured cellular foam (MCF) silica, and they were applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Among the catalysts tested, palladium catalyst supported on SO_3H-functionalized MCF silica was most active in the reaction [14].

It has been reported that hydroxyl groups on the surface of silica play an important role in grafting silica particles with surface modification agents [19-23]. It is known that concentration and distribution of hydroxyl groups on the surface of silica can be tuned by adjusting calcination temperature of silica [24]. Therefore, it is expected that the degree of surface functionalization can be controlled by changing calcination temperature of silica when silica particles are grafted with the surface modification agents.

In this work, palladium catalysts supported on SO_3H-functionalized MCF silica (Pd/SO_3H-MCF) were prepared with a variation of calcination temperature of MCF silica. They were then applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen, with the aim of utilizing palladium and SO_3H-functional-

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ized MCF silica as an active metal component and as an alternate acid source, respectively. The effect of calcination temperature of MCF silica on the catalytic performance of Pd/SO_3H-MCF catalysts in the direct synthesis of hydrogen peroxide was investigated.

EXPERIMENTAL

1. Catalyst Preparation

MCF silica was synthesized according to the reported method [25,26], and they were calcined at various temperatures (450, 550, 650, 750, 850, and 950 °C). SO_3H-functionalized MCF silica (SO_3H-MCF) was prepared by a grafting method, according to the similar method reported in the literature [17-19]. Palladium catalyst supported on SO_3H-functionalized MCF silica (Pd/SO_3H-MCF) was then prepared by an ion-exchange method. Pd/SO_3H-MCF was denoted as Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950), where T represented calcination temperature of MCF silica in Celsius.

Typical procedures for the preparation of Pd/SO_3H-MCF-750 catalyst are as follows. 10 g of PEO-PPO-PEO triblock copolymer (Pluronic P123, BASF) was dissolved in 375 ml of 1.6 M HCl aqueous solution at 40 °C. 4.6 ml of 1,3,5-trimethylbenzene (Mesitylene, Sigma-Aldrich) was then added into the mixed solution. After the solution was stirred at 40 °C for 1 h, 24.1 ml of tetraethyl orthosilicate (TEOS, Sigma-Aldrich) was added to it. The resulting mixture was stirred at 40 °C for 20 h and maintained at 130 °C for 20 h under static condition. After the solid product was filtered and washed with distilled water, it was dried at room temperature. The solid product was calcined at 750 °C for 5 h to yield MCF-750 silica. MCF-750 silica was then dispersed in anhydrous toluene (Sigma-Aldrich) with constant stirring under nitrogen atmosphere. After 3-mercaptopropyltrimethoxy silane (3-MPTMS, Sigma-Aldrich) was added into the dispersed solution, the mixture was stirred for 1 day. A solid recovered from the mixture by filtration was washed with toluene and dried overnight at 80 °C. Thiol (-SH) group on the surface of MCF-750 silica was converted into sulfonic acid (-SO_3H) group by treating the solid with an aqueous solution of HNO_3. For this, the solid was dispersed in 20% HNO_3 solution and then mixed with 69% HNO_3 solution. The mixture was stirred for 1 day at room temperature. After the resulting solid was washed with distilled water, it was dried overnight at 80 °C to obtain SO_3H-MCF-750 support. SO_3H-MCF-750 was then added to an aqueous solution of $Pd(NO_3)_2$ (Sigma-Aldrich) with constant stirring. A solid product recovered by filtration was washed with distilled water and dried at 80 °C to yield Pd/SO_3H-MCF-750 catalyst. The Pd loading was fixed at 0.5 wt%.

2. Catalyst Characterization

N_2 adsorption-desorption isotherm of the catalyst was obtained with an ASAP-2010 instrument (Micromeritics), and pore size distribution was determined by the BJH (Barrett-Joyner-Hallender) method applied to the desorption branch of the isotherm. X-ray diffraction (XRD) pattern of the catalyst was confirmed by XRD measurement (Rigaku, D-Max2500-PC) using Cu-Kα radiation operated at 50 kV and 100 mA. Chemical state of the catalyst was examined by ^{13}C CP-MAS NMR analysis (Bruker, AVANCE 400 WB) to ensure the successful grafting of -SO_3H group on the surface of MCF silica [17-19]. Acid-base titration [27,28] was carried out to measure the acid amount of catalyst. In a typical measurement, 0.1 g of catalyst was dispersed in 30 ml of 0.1 M KCl solution. The mixture was stirred for 20 min and then titrated with 0.2 M KOH solution in the presence of phenolphthalein.

3. Direct Synthesis of Hydrogen Peroxide from Hydrogen and Oxygen

Hydrogen peroxide was directly synthesized from hydrogen and oxygen in an autoclave reactor in the absence of acid additive. 80 ml of methanol and 6.32 mg of sodium bromide were charged into the reactor. 1 g of each catalyst was then added into the reactor. H_2/N_2 (25 mol% H_2) and O_2/N_2 (50 mol% O_2) were bubbled through the reaction medium under vigorous stirring (1,000 rpm). H_2/O_2 ratio in the feed stream was fixed at 0.4, and total feed rate was maintained at 44 ml/min. Catalytic reaction was carried out at 28 °C and 10 atm for 6 h. In the catalytic reaction, mixed gases diluted with an inert gas (H_2/N_2 (25 mol% H_2) and O_2/N_2 (50 mol% O_2)) and an autoclave reactor equipped with a flashback arrestor as well as a safety valve were used in order to solve the safety problem. Unreacted hydrogen was analyzed with a gas chromatograph (Younglin, ACME 6000) equipped with a TCD. Concentration of hydrogen peroxide was determined by an iodometric titration method [29]. Conversion of hydrogen and selectivity for hydrogen peroxide were calculated according to the following equations. Yield for hydrogen peroxide was calculated by multiplying conversion of hydrogen and selectivity for hydrogen peroxide.

$$\text{Conversion of hydrogen} = \frac{\text{moles of hydrogen reacted}}{\text{moles of hydrogen supplied}}$$

$$\text{Selectivity for hydrogen peroxide} = \frac{\text{moles of hydrogen peroxide formed}}{\text{moles of hydrogen reacted}}$$

RESULTS AND DISCUSSION

1. Catalyst Characterization

Fig. 1 shows the N_2 adsorption-desorption isotherms and pore size distributions of Pd/SO_3H-MCF-550, Pd/SO_3H-MCF-750, and Pd/SO_3H-MCF-950. Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950) catalysts showed IV-type isotherms with H1-type hysteresis loops, as reported in the literature [25]. However, Pd/SO_3H-

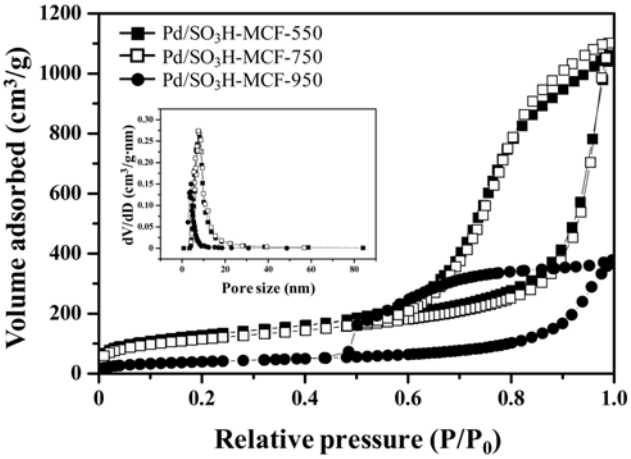

Fig. 1. N_2 adsorption-desorption isotherms and pore size distributions of Pd/SO_3H-MCF-550, Pd/SO_3H-MCF-750, and Pd/SO_3H-MCF-950.

Table 1. Surface area, pore volume, and average pore size of MCF-T and Pd/SO_3H-MCF-T

	Surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]	Average pore size (nm)[c]
MCF-450	629.1	1.96	8.0
MCF-550	559.2	1.93	7.9
MCF-650	542.2	2.18	9.5
MCF-750	436.6	1.98	10.6
MCF-850	413.7	1.83	9.3
MCF-950	178.2	0.69	4.1
Pd/SO_3H-MCF-450	475.0	1.62	7.8
Pd/SO_3H-MCF-550	459.0	1.65	8.8
Pd/SO_3H-MCF-650	433.8	1.92	9.5
Pd/SO_3H-MCF-750	407.6	1.90	11.0
Pd/SO_3H-MCF-850	358.3	1.69	9.8
Pd/SO_3H-MCF-950	142.0	0.59	4.2

[a]Calculated by the BET (Brunauer-Emmett-Teller) equation
[b]BJH (Barrett -Joyner-Hallender) desorption pore volume
[c]BJH (Barrett -Joyner-Hallender) desorption average pore diameter

MCF-950 catalyst exhibited slightly different N_2 adsorption-desorption isotherm and pore size distribution from those of the other catalysts, because shrinkage of pore structure of MCF silica occurred by a condensation reaction when MCF silica was calcined at high temperature [24]. It was observed that N_2 adsorption-desorption isotherm and pore size distribution of Pd/SO_3H-MCF-T catalyst were similar to those of corresponding MCF-T silica, although these are not shown here. This supports that pore structure of MCF silica was still maintained even after the grafting of -SO_3H group on the surface of MCF silica and the loading of palladium.

Detailed textural properties of MCF-T silicas and Pd/SO_3H-MCF-T catalysts are summarized in Table 1. It was observed that surface area and pore volume of Pd/SO_3H-MCF-T catalyst were lower than those of corresponding MCF-T silica due to the grafting of -SO_3H group and the loading of palladium. However, Pd/SO_3H-MCF-T catalysts still retained high surface areas and large pore volumes. Surface area of Pd/SO_3H-MCF-T catalysts decreased with increasing calcination temperature of MCF silica, while pore volume and average pore size of Pd/SO_3H-MCF-T catalysts showed volcano-shape trends with respect to calcination temperature of MCF silica. However, Pd/SO_3H-MCF-T catalysts except for Pd/SO_3H-MCF-950 still retained unique pore characteristics of MCF silica [25]. Pd/SO_3H-MCF-950 exhibited much lower surface area, pore volume, and average pore size than the other Pd/SO_3H-MCF-T catalysts due to the shrinkage of pore structure of MCF silica, as mentioned earlier.

Fig. 2 shows the XRD patterns of Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950) catalysts. Pd/SO_3H-MCF-T catalysts showed no diffraction peaks due to an amorphous nature of MCF silica [26]. This indicates that calcination at 450-950 °C had negligible effect on the phase transition of silica. Furthermore, no characteristic diffraction peak for PdO (JCPDS 43-1024) was observed in all the Pd/SO_3H-MCF-T catalysts, implying that palladium species were finely dispersed on the surface of SO_3H-MCF-T supports.

Fig. 3 shows the ^{13}C CP-MAS NMR spectra of Pd/SO_3H-MCF-550 and Pd/SO_3H-MCF-750. Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950) catalysts showed three resonance peaks at δ=

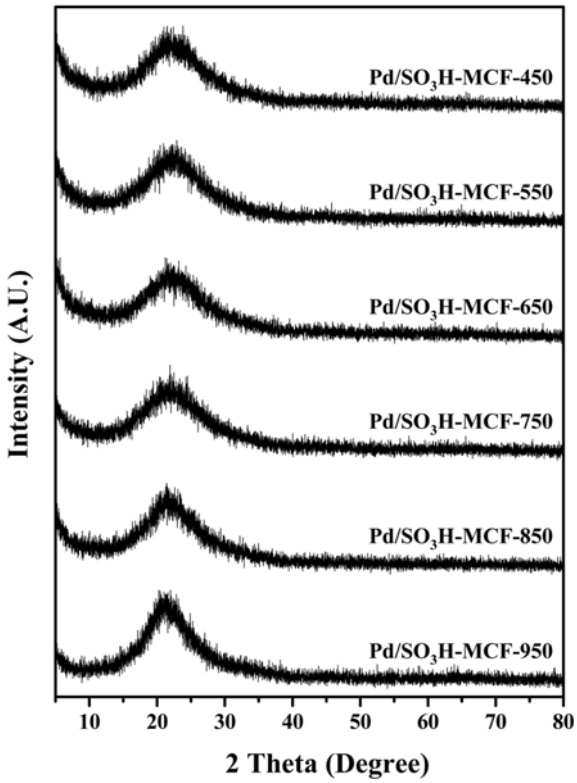

Fig. 2. XRD patterns of Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950) catalysts.

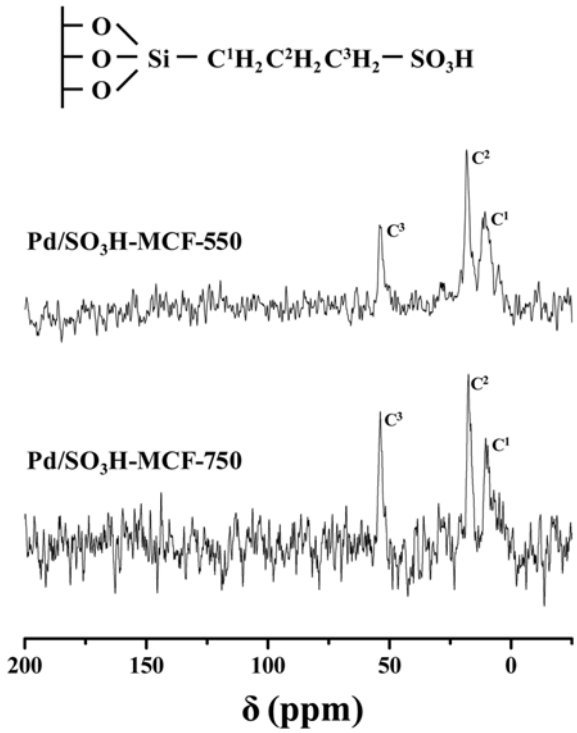

Fig. 3. ^{13}C CP-MAS NMR spectra of Pd/SO_3H-MCF-550 and Pd/SO_3H-MCF-750.

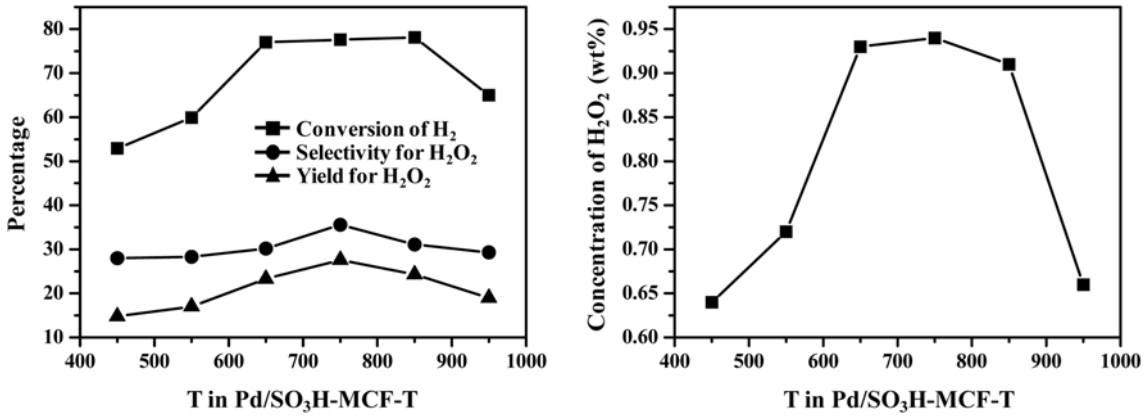

Fig. 4. Catalytic performance of Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950) catalysts in the direct synthesis of hydrogen peroxide from hydrogen and oxygen after a 6 h-reaction.

11.2 (C^1), 18.3 (C^2), and 54.1 (C^3) ppm. These resonance peaks were attributed to different carbon atoms in 3-MPTMS; C^1 carbon bonded to Si atom, C^2 carbon of propyl chain, and C^3 carbon bonded to -SO_3H group [17-19]. No characteristic peak was observed at 29 ppm in all the catalysts. This indicates that -SH group was completely oxidized to -SO_3H group [17-19]. Moreover, no peaks were detected at 40 ppm and 23 ppm. This implies that no disulfide species were formed under our preparation conditions [17-19]. These results indicate that -SO_3H group was successfully grafted on the surface of MCF-T silicas.

2. Catalytic Performance in the Direct Synthesis of Hydrogen Peroxide

Fig. 4 shows the catalytic performance of Pd/SO_3H-MCF-T (T= 450, 550, 650, 750, 850, and 950) catalysts in the direct synthesis of hydrogen peroxide from hydrogen and oxygen, plotted as a function of calcination temperature of MCF silica. Conversion of hydrogen, selectivity for hydrogen peroxide, and yield for hydrogen peroxide showed volcano-shaped curves with respect to calcination temperature of MCF silica. Final concentration of hydrogen peroxide after a 6 h-reaction also showed a volcano-shaped curve with respect to calcination temperature of MCF silica. Among the catalysts tested, Pd/SO_3H-MCF-750 catalyst exhibited the best catalytic performance in terms of selectivity for hydrogen peroxide, yield for hydrogen peroxide, and final concentration of hydrogen peroxide.

3. Acid Property of Pd/SO_3H-MCF Catalysts

In previous works [11,14], it was revealed that acid density (or surface acidity) of the catalysts served as a crucial factor determining the catalytic performance in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. To elucidate the different catalytic performance of Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950) catalysts, the acid amount of Pd/SO_3H-MCF-T catalysts was measured by an acid-base titration [27,28]. Acid density of Pd/SO_3H-MCF-T catalysts was then calculated by dividing acid amount of Pd/SO_3H-MCF-T catalysts by surface area of the catalysts. Acid amount and acid density of Pd/SO_3H-MCF-T catalysts are summarized in Table 2. Acid amount of Pd/SO_3H-MCF-T catalysts decreased with increasing calcination temperature of MCF silica. It has been reported that the amount of hydroxyl groups of silica is closely related to the amount of functional groups of grafted surface modification agents, because hydroxyl groups of silica react with alkoxy groups of surface modification agents [19-22]. Therefore, it is believed that the decrease of acid amount of Pd/SO_3H-MCF-T catalysts with increasing calcination temperature was attributed to the decrease of the amount of hydroxyl groups of MCF silica.

Table 2. Acid amount and acid density of Pd/SO_3H-MCF-T

Catalyst	Acid amount (mmol-H^+/g)	Acid density (μmol-H^+/m^2)
Pd/SO_3H-MCF-450	0.56	1.18
Pd/SO_3H-MCF-550	0.54	1.18
Pd/SO_3H-MCF-650	0.52	1.20
Pd/SO_3H-MCF-750	0.50	1.23
Pd/SO_3H-MCF-850	0.43	1.21
Pd/SO_3H-MCF-950	0.17	1.20

Interestingly, the acid density of Pd/SO_3H-MCF-T catalysts showed a volcano-shaped trend with respect to calcination temperature of MCF silica. It has been reported that the number density of free silanols, which were highly accessible to the surface modification agents, showed a volcano-shaped trend with respect to calcination temperature [21,24]. Therefore, it can be inferred that acid density of Pd/SO_3H-MCF-T catalysts was influenced by the number density of free silanols of MCF-T silicas. Among the Pd/SO_3H-MCF-T catalysts, Pd/SO_3H-MCF-750 catalyst exhibited the highest acid density.

4. Effect of Acid Density on the Catalytic Performance

Experimental results revealed that there was no reliable correlation between yield for hydrogen peroxide over Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950) catalysts and acid amount of the catalysts. However, yield for hydrogen peroxide over Pd/SO_3H-MCF-T catalysts was closely related to the acid density of the catalysts, as shown in Fig. 5. Yield for hydrogen peroxide increased with increasing acid density of Pd/SO_3H-MCF-T catalysts. Among the catalysts tested, Pd/SO_3H-MCF-750 catalyst with the highest acid density showed the highest yield for hydrogen peroxide. This indicates that acid density of Pd/SO_3H-MCF-T catalysts played an important role in determining the catalytic performance in the direct synthesis of hydrogen peroxide from hydrogen and oxygen.

As mentioned, it has been reported that acid additives enhance

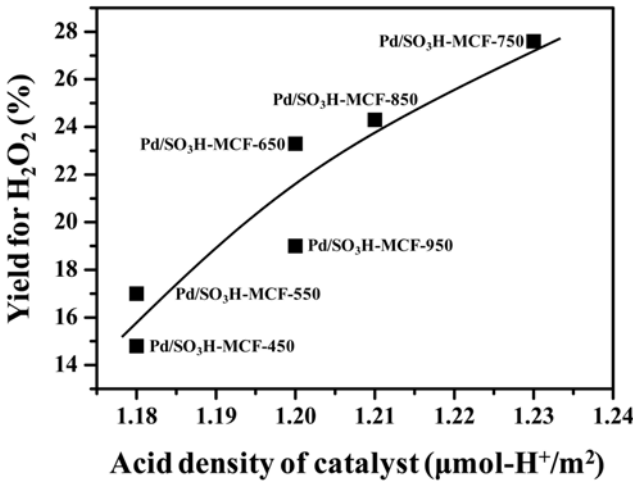

Fig. 5. A correlation between yield for hydrogen peroxide over Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950) catalysts and acid density of the catalysts.

the selectivity for hydrogen peroxide because acid additives prevent the decomposition of hydrogen peroxide by surrounding hydrogen peroxide with its protons [1,2]. It is expected that effective surround of hydrogen peroxide by protons of Pd/SO_3H-MCF-T catalysts is possible, when acid density (compactness of protons) of Pd/SO_3H-MCF-T catalysts is high. Therefore, acid density of Pd/SO_3H-MCF-T catalysts served as a crucial factor determining the catalytic performance in the direct synthesis of hydrogen peroxide. It is concluded that the improved yield for hydrogen peroxide over Pd/SO_3H-MCF-T catalysts was attributed to the enhanced acid density of the catalysts.

CONCLUSIONS

Palladium catalysts supported on SO_3H-functionalized MCF silica (Pd/SO_3H-MCF-T (T=450, 550, 650, 750, 850, and 950)) were applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Conversion of hydrogen, selectivity for hydrogen peroxide, and yield for hydrogen peroxide showed volcano-shaped curves with respect to calcination temperature of MCF silica. Acid density of Pd/SO_3H-MCF-T catalysts also showed a volcano-shaped trend with respect to calcination temperature of MCF silica. Yield for hydrogen peroxide increased with increasing acid density of Pd/SO_3H-MCF-T catalysts. Among the catalysts tested, Pd/SO_3H-MCF-750 catalyst with the highest acid density showed the highest yield for hydrogen peroxide. We conclude that the enhanced yield for hydrogen peroxide over Pd/SO_3H-MCF-T catalysts was attributed to the improved acid density of the catalysts. Pd/SO_3H-MCF-T catalysts efficiently served as an alternate acid source and as an active metal catalyst in the direct synthesis of hydrogen peroxide.

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