



Direct synthesis of hydrogen peroxide from hydrogen and oxygen over insoluble Cs_{2.5}H_{0.5}PW₁₂O₄₀ heteropolyacid supported on Pd/MCF

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ABSTRACT

Insoluble Cs_{2.5}H_{0.5}PW₁₂O₄₀ heteropolyacid supported on Pd/MCF (CsPW/Pd/MCF-X (X = 10.0, 21.7, 35.7, 52.6, and 68.9)) was prepared with a variation of Cs_{2.5}H_{0.5}PW₁₂O₄₀ content (X, wt%) for use in direct synthesis of hydrogen peroxide from hydrogen and oxygen. High catalytic performance of CsPW/Pd/MCF-X catalysts compared to Pd/MCF catalyst was attributed to the enhanced acid property of CsPW/Pd/MCF-X catalysts. Selectivity for hydrogen peroxide and yield for hydrogen peroxide over CsPW/Pd/MCF-X catalysts showed a volcano-shaped curve with respect to Cs_{2.5}H_{0.5}PW₁₂O₄₀ content. Acidity of the catalysts also showed a volcano-shaped trend with respect to Cs_{2.5}H_{0.5}PW₁₂O₄₀ content. It was revealed that yield for hydrogen peroxide increased with increasing acidity of CsPW/Pd/MCF-X catalyst. Acidity of CsPW/Pd/MCF-X catalyst played a crucial role in determining the catalytic performance in the direct synthesis of hydrogen peroxide.

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1. Introduction

Hydrogen peroxide (H₂O₂) has been widely utilized in various areas, including pulp industry, textile industry, and wastewater treatment [1,2]. Hydrogen peroxide has also been used as a clean and strong oxidant in green chemical synthesis such as epoxidation of propylene to propylene oxide [3]. Hydrogen peroxide currently provided in the industrial market is mostly produced through the anthraquinone 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 [4–19].

In the direct synthesis of hydrogen peroxide from hydrogen and oxygen, several undesired reactions occur simultaneously together with selective oxidation of hydrogen to hydrogen peroxide (H₂ + O₂ → H₂O₂) [1,2]. These undesired reactions include formation of water (H₂ + 0.5O₂ → H₂O), hydrogenation of hydrogen peroxide (H₂O₂ + H₂ → 2H₂O), and decomposition of hydrogen peroxide (H₂O₂ → H₂O + 0.5O₂). All these reactions are known to be thermodynamically favorable and highly exothermic [1,2]. It has been reported that formation of water and hydrogenation of

hydrogen peroxide are thermodynamically more favorable than selective oxidation of hydrogen to hydrogen peroxide [1,2]. Consequently, selectivity for hydrogen peroxide in the direct synthesis of hydrogen peroxide is limited by these undesired reactions. Therefore, many attempts have been made to increase the selectivity for hydrogen peroxide in the direct synthesis of hydrogen peroxide [10–13].

Various noble metals such as palladium [6–13], palladium–gold [14–17], and palladium–platinum [18,19] have been used as catalysts in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Among these catalysts, palladium is known to be the most efficient catalyst in the direct synthesis of hydrogen peroxide [6–13]. Palladium catalyst has been supported on various materials such as silica, alumina, and carbon for effective dispersion of active metal component [7].

Acids and halides have been used as additives to enhance the selectivity for hydrogen peroxide in the direct synthesis of hydrogen peroxide from hydrogen and oxygen [10–13]. It has been reported that acids and halides prevent the decomposition of hydrogen peroxide and inhibit the formation of water [1,2,10–13]. However, acid additives cause the dissolution of active metal component from the supported catalyst and accelerate the corrosion of reactor. Therefore, acidic supports have been investigated in the direct synthesis of hydrogen peroxide as an alternate acid additive [20–22].

Heteropolyacids (HPAs) are inorganic acids. It is known that acid strength of HPAs is stronger than that of conventional solid acids

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[23–27]. Therefore, HPAs have been investigated as solid acid catalysts in several acid-catalyzed reactions [23–25]. However, most of HPAs are highly soluble in polar solvents and have low surface area ($<10\text{ m}^2/\text{g}$) [23–25]. To overcome these problems, insoluble HPA catalysts prepared by exchanging protons with certain cations have been utilized in several catalytic reactions [23,24]. It has been reported that HPA salts with large cations such as K^+ , Rb^+ , Cs^+ , and NH_4^+ are insoluble, and have high surface area and porous structure by forming a tertiary structure [23,24]. In our previous work [21], it was observed that palladium-exchanged insoluble HPA catalysts showed high catalytic performance in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. However, it was difficult to separate palladium-exchanged insoluble HPA catalysts from polar solvents because insoluble HPAs were composed of very fine particles with an average size of ca. 10 nm [24].

Mesoporous silicas have been utilized in many fields of science and engineering, including catalysis, adsorption, and separation, because they have uniform pore size, high surface area, and large pore volume [28–32]. Especially, it has been reported that mesostructured cellular foam (MCF) silica exhibits an aerogel-like 3-dimensional pore structure with large pores in the range of 10–50 nm [28–30]. Due to its unique pore characteristics, MCF silica has been used as an efficient support for covalent immobilization of large molecules such as enzymes [30]. In our previous work [22], palladium catalysts supported on SO_3H -functionalized mesoporous silicas were prepared using MCM-41, MCM-48, MSU-1, SBA-15, and MCF silica, and they were applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Among the catalysts tested, Pd/ SO_3H -MCF was found to be the most active catalyst in the reaction [22]. Thus, MCF silica served as an efficient supporting material in the direct synthesis of hydrogen peroxide.

In this work, insoluble $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ heteropolyacid supported on Pd/MCF was prepared with a variation of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content. The prepared catalyst was applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen, with an aim of utilizing palladium and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ as an active metal component and as an alternate acid source, respectively. The effect of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content on the catalytic performance of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$ in the direct synthesis of hydrogen peroxide was investigated. A correlation between acidity and catalytic performance of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$ catalysts was then established.

2. Experimental

2.1. Catalyst preparation

MCF silica was synthesized according to the reported method [28–30]. Pd/MCF was prepared by an incipient wetness impregnation method. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropolyacid supported on Pd/MCF ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$) was prepared by an incipient wetness impregnation method with a variation of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ content. Insoluble $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ heteropolyacid supported on Pd/MCF catalyst ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$) was then prepared by an ion-exchange method, in order to take advantage of high surface area and large acidity of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ [23,24].

Typical procedures for the preparation of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$ catalyst are as follows. Palladium nitrate ($\text{Pd}(\text{NO}_3)_2$, Sigma–Aldrich) was supported onto MCF silica. The impregnated solid was dried overnight at 80°C , and then it was calcined at 500°C for 3 h. The palladium loading was fixed at 0.5 wt%. After impregnating $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Sigma–Aldrich) onto Pd/MCF, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$ was dried overnight at 80°C and calcined at 300°C for 2 h. $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$ was dispersed in distilled water with constant stirring. An aqueous solution of

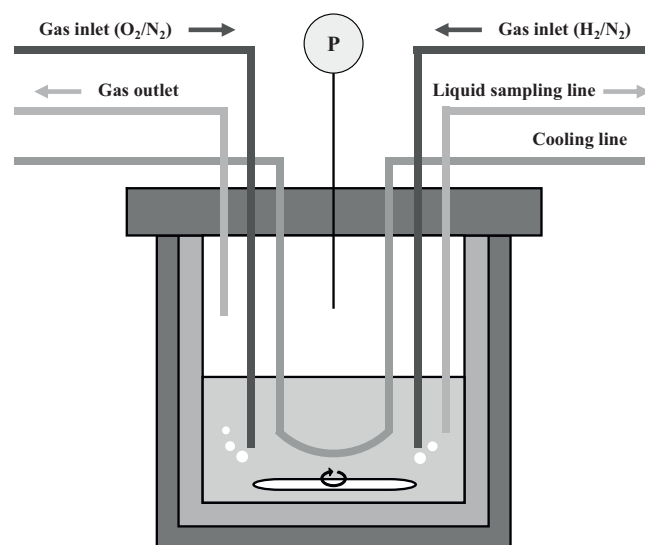


Fig. 1. Scheme of reaction system.

cesium nitrate (CsNO_3 , Sigma–Aldrich) was added into the dispersed solution, and the mixture was stirred for 12 h. After filtering and washing a solid product with distilled water, the solid was dried overnight at 80°C , and finally, it was calcined at 300°C for 2 h to yield $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$ catalyst. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content (X) in the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$ catalysts was adjusted to 10.0, 21.7, 35.7, 52.6, and 68.9 wt%. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{Pd}/\text{MCF}$ catalysts were denoted as CsPW/Pd/MCF-X (X = 10.0, 21.7, 35.7, 52.6, and 68.9).

2.2. Catalyst characterization

$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content in the catalyst was measured by ICP–AES analysis (Shimadzu, ICPS–7500). Dispersion of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ on the supported catalyst was examined by TEM analysis (Jeol, JEM–3000F). 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 (Barret–Joyner–Hallender) method applied to the desorption branch of the isotherm. Infrared spectrum of the catalyst was obtained with a FT–IR spectrometer (Nicolet, Nicolet 6700). X-ray diffraction (XRD) pattern of the catalyst was confirmed by XRD measurement (Rigaku, D–Max2500–PC) using $\text{Cu-K}\alpha$ radiation operated at 50 kV and 100 mA. NH_3 -TPD (BEL Japan, BELCAT–B) experiment was carried out in order to measure the acidity of the catalyst. 0.05 g of each catalyst charged into the TPD apparatus was pretreated at 200°C for 1 h with a stream of He (50 ml/min). 5 mol% NH_3/He (50 ml/min) was introduced into the reactor at 50°C for 30 min in order to saturate acid sites of the catalyst with NH_3 . Physisorbed NH_3 was removed at 100°C for 1 h under a flow of He (50 ml/min). After cooling the catalyst, furnace temperature was increased from 50 to 850°C at a heating rate of $5^\circ\text{C}/\text{min}$ under a flow of He (30 ml/min). Desorbed NH_3 was detected using a TCD (thermal conductivity detector).

2.3. Direct synthesis of hydrogen peroxide

Direct synthesis of hydrogen peroxide from hydrogen and oxygen was carried out in an autoclave reactor in the absence of acid additive. Fig. 1 shows the scheme of reaction system. 80 ml of methanol and 6.32 mg of sodium bromide were charged into the reactor. Prescribed amount of each catalyst was then added into the reactor to keep the identical level of palladium amount in each

Table 1
CsPW content, surface area, pore volume, average pore size, and acidity of CsPW/Pd/MCF-X catalysts.

Catalyst	CsPW content (wt%)	Surface area (m ² /g) ^a	Pore volume (cm ³ /g) ^b	Average pore size (nm) ^c	Acidity (μmol NH ₃ /g)
Pd/MCF	–	577.8	1.61	8.3	52.8
CsPW/Pd/MCF-10.0	7.0	516.1	1.43	8.1	104.7
CsPW/Pd/MCF-21.7	18.0	460.8	1.30	8.2	105.8
CsPW/Pd/MCF-35.7	31.8	406.4	1.08	8.0	106.2
CsPW/Pd/MCF-52.6	51.9	307.9	0.83	8.1	101.4
CsPW/Pd/MCF-68.9	68.6	245.2	0.60	8.2	74.1

^a Calculated by the BET (Brunauer–Emmett–Teller) equation.

^b BJH (Barret–Joyner–Hallender) desorption pore volume.

^c BJH (Barret–Joyner–Hallender) desorption average pore diameter.

run. H₂/N₂ (25 mol% H₂) and O₂/N₂ (50 mol% O₂) were bubbled through the reaction medium under vigorous stirring (1000 rpm). H₂/O₂ 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 (H₂/N₂ (25 mol% H₂) and O₂/N₂ (50 mol% O₂)) 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 using a gas chromatograph (Younglin, ACME 6000) equipped with a TCD. Concentration of hydrogen peroxide was determined by an iodometric titration method [33]. 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.

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

Selectivity for hydrogen peroxide

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

2.4. Hydrogenation of hydrogen peroxide

80 ml of methanol, 6.32 mg of sodium bromide, and 1.56 g of CsPW/Pd/MCF-35.7 catalyst were charged into the reactor. 3 ml of 30 wt% hydrogen peroxide was then added. H₂/N₂ (25 mol% H₂) and N₂ were bubbled through the reaction medium under vigorous stirring (1000 rpm). H₂/N₂ ratio in the feed stream was fixed at 0.1, and total feed rate was maintained at 44 ml/min. The reaction was carried out at 28 °C and 10 atm for 6 h. Concentration of hydrogen peroxide was determined by an iodometric titration method [33]. Degree of hydrogenation of H₂O₂ was calculated according to the following equation. For comparison, hydrogenation of hydrogen peroxide was also carried out using 1 g of Pd/MCF catalyst under the same reaction conditions.

Degree of hydrogenation of H₂O₂

$$= \frac{\text{moles of hydrogen peroxide hydrogenated}}{\text{moles of hydrogen peroxide supplied}}$$

2.5. Decomposition of hydrogen peroxide

80 ml of methanol, 6.32 mg of sodium bromide, and 1.56 g of CsPW/Pd/MCF-35.7 catalyst were charged into the reactor. 3 ml of 30 wt% hydrogen peroxide was then added. N₂ (44 ml/min) was bubbled through the reaction medium under vigorous stirring (1000 rpm). The reaction was carried out at 28 °C and 10 atm for 6 h. Concentration of hydrogen peroxide was determined by an iodometric titration method [33]. Degree of decomposition of H₂O₂

was calculated according to the following equation. For comparison, decomposition of hydrogen peroxide was also carried out using 1 g of Pd/MCF catalyst under the same reaction conditions.

Degree of decomposition of H₂O₂

$$= \frac{\text{moles of hydrogen peroxide decomposed}}{\text{moles of hydrogen peroxide supplied}}$$

3. Results and discussion

3.1. Catalyst characterization

Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW) contents in the CsPW/Pd/MCF-X (X = 10.0, 21.7, 35.7, 52.6, and 68.9) catalysts determined by ICP-AES analyses are listed in Table 1. Cs_{2.5}H_{0.5}PW₁₂O₄₀ contents in the CsPW/Pd/MCF-X were in good agreement with the designed values. This indicates that CsPW/Pd/MCF-X catalysts were successfully prepared as attempted in this work.

Fig. 2 shows the TEM images of Pd/MCF and CsPW/Pd/MCF-X (X = 10.0, 21.7, 35.7, 52.6, and 68.9) catalysts. Pore structure and pore size of CsPW/Pd/MCF-X catalysts were almost identical to those of Pd/MCF. CsPW/Pd/MCF-X catalysts exhibited a disordered pore structure with large pores in the range of 8–10 nm, in agreement with the reported results [28,29]. This implies that MCF silica was successfully prepared and pore structure of MCF silica was still maintained even after the loading of palladium and Cs_{2.5}H_{0.5}PW₁₂O₄₀. It was also observed that the amount of Cs_{2.5}H_{0.5}PW₁₂O₄₀ agglomerates (dark spots) on the catalyst increased with increasing Cs_{2.5}H_{0.5}PW₁₂O₄₀ content. Furthermore, small particles of palladium species with an average size of ca. 10 nm were observed in the TEM images of the catalysts, indicating that palladium species were finely dispersed on the surface of MCF silica. Palladium dispersion on the catalysts was in the range of 10.1–12.9% with no great difference.

Fig. 3 shows the N₂ adsorption–desorption isotherms and pore size distributions of Pd/MCF, CsPW/Pd/MCF-35.7, and CsPW/Pd/MCF-68.9. N₂ adsorption–desorption isotherm and pore size distribution of CsPW/Pd/MCF-X catalysts were similar to those of Pd/MCF. CsPW/Pd/MCF-X catalysts showed IV-type isotherms with H1-type hysteresis loops, as reported in the previous works [28–30]. This result also supports that pore structure of MCF silica was still maintained even after the loading of palladium and Cs_{2.5}H_{0.5}PW₁₂O₄₀ on the surface of MCF silica, as evidenced by TEM images. Detailed textural properties of CsPW/Pd/MCF-X catalysts are summarized in Table 1. It was observed that surface area and pore volume of CsPW/Pd/MCF-X catalysts monotonically decreased with increasing Cs_{2.5}H_{0.5}PW₁₂O₄₀ content. However, no noticeable difference in average pore size of CsPW/Pd/MCF-X catalysts was observed. This may be attributed to the formation of Cs_{2.5}H_{0.5}PW₁₂O₄₀ aggregates on the pore walls, resulting in blocking the pore of Pd/MCF [34], because crystal size of Cs_{2.5}H_{0.5}PW₁₂O₄₀ was similar to pore size of Pd/MCF [24].

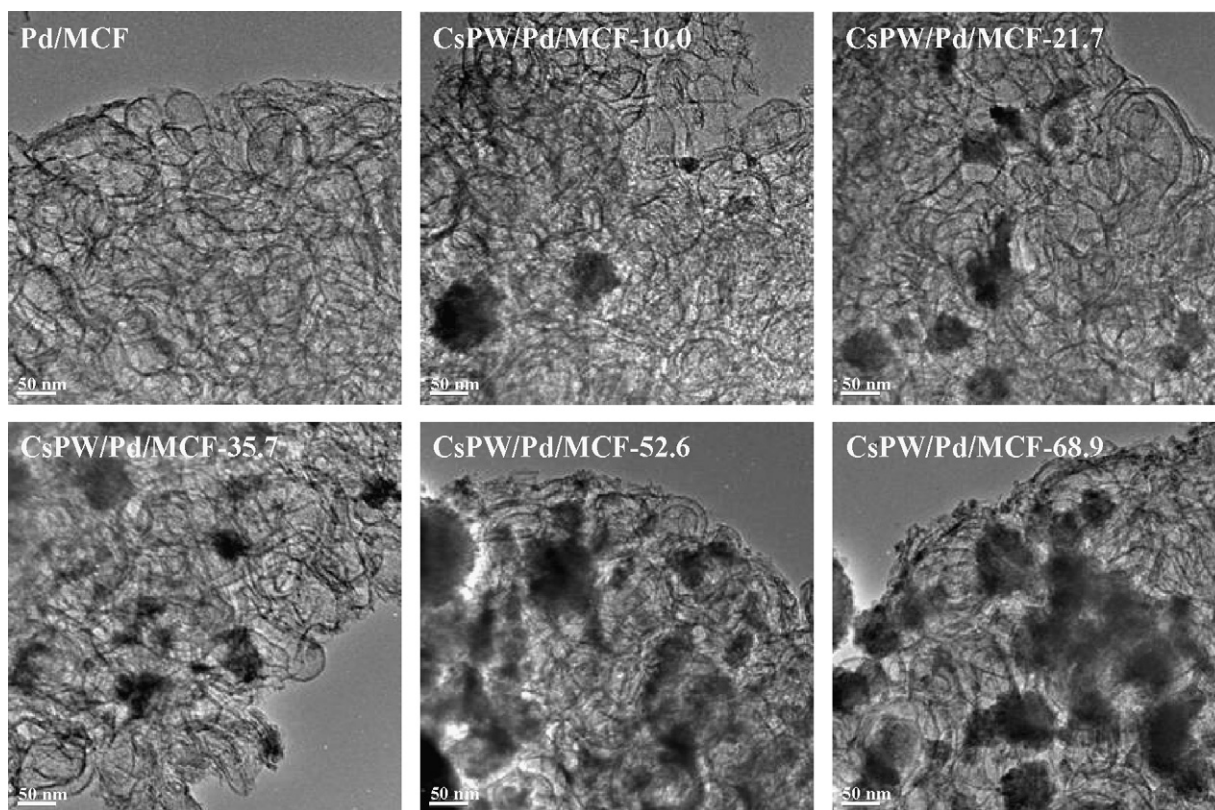


Fig. 2. TEM images of Pd/MCF and CsPW/Pd/MCF- X ($X = 10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts.

Fig. 4 shows the FT-IR spectra of Pd/MCF, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW), and CsPW/Pd/MCF- X ($X = 10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts. Pd/MCF showed broad bands at around $1000\text{--}1300$ and 800 cm^{-1} , which were attributed to Si–O–Si bands [35]. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ exhibited four characteristic IR bands at 1080 (P–O), 985 (W=O), 890 (interoctahedral W–O–W), and 810 (intraoctahedral W–O–W) cm^{-1} , corresponding to the characteristic IR bands of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [36]. In the case of CsPW/Pd/MCF-10.0 and CsPW/Pd/MCF-21.7 catalysts, the characteristic IR bands at $1080, 985, 890,$ and 810 cm^{-1} were not clearly observed, because $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content was low. However, these four characteristic IR bands were observed in the CsPW/Pd/MCF-35.7, CsPW/Pd/MCF-52.6, and CsPW/Pd/MCF-68.9 catalysts. Further-

more, peak intensities increased with increasing $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content in the catalysts. This indicates that the primary structure of HPA was still maintained even after the impregnation on Pd/MCF.

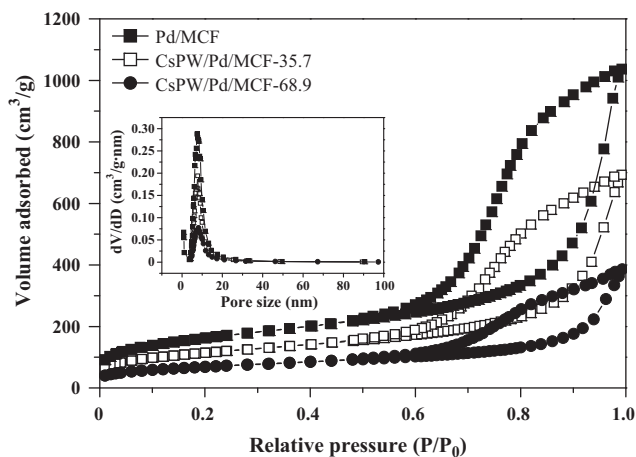


Fig. 3. N_2 adsorption–desorption isotherms and pore size distributions of Pd/MCF, CsPW/Pd/MCF-35.7, and CsPW/Pd/MCF-68.9.

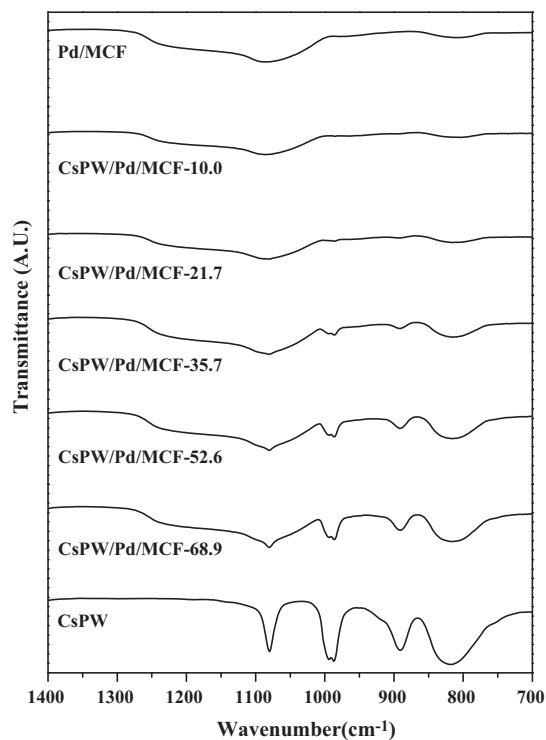


Fig. 4. FT-IR spectra of Pd/MCF, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW), and CsPW/Pd/MCF- X ($X = 10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts.

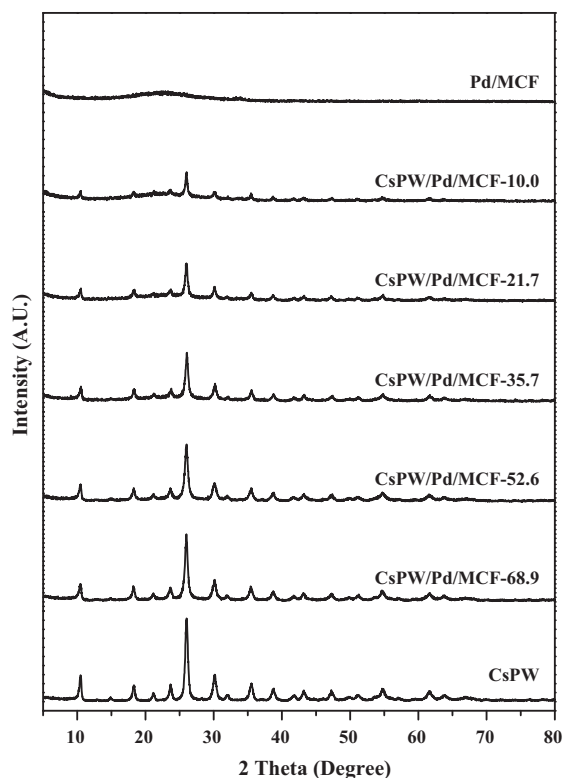


Fig. 5. XRD patterns of Pd/MCF, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW), and CsPW/Pd/MCF- X ($X=10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts.

Fig. 5 shows the XRD patterns of Pd/MCF, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW), and CsPW/Pd/MCF- X ($X=10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts. Pd/MCF showed no diffraction peaks due to an amorphous nature of MCF silica [35]. The characteristic diffraction peaks for $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ were observed in all the CsPW/Pd/MCF- X catalysts, and peak intensities increased with increasing $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content in the catalysts, as reported in the previous work [34]. This result also supports that CsPW/Pd/MCF- X catalysts were successfully prepared in this work.

3.2. Catalytic performance in the direct synthesis of hydrogen peroxide

Fig. 6 shows the catalytic performance of CsPW/Pd/MCF- X ($X=10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts in the direct synthe-

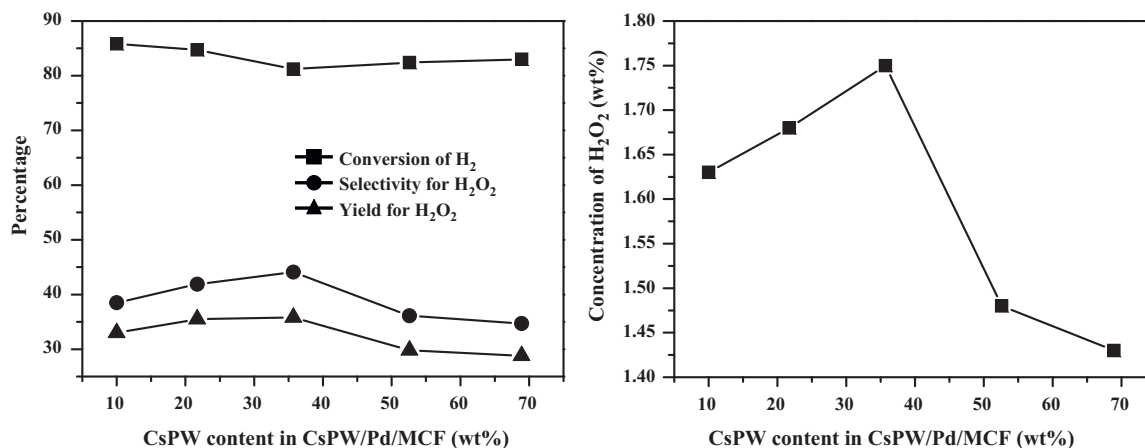


Fig. 6. Catalytic performance of CsPW/Pd/MCF- X ($X=10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts in the direct synthesis of hydrogen peroxide from hydrogen and oxygen after a 6-h reaction.

sis of hydrogen peroxide from hydrogen and oxygen, plotted as a function of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content. Conversion of hydrogen over the catalysts showed no great difference, while selectivity for hydrogen peroxide exhibited a volcano-shaped curve with respect to $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content. As a consequence, yield for hydrogen peroxide showed a volcano-shaped curve with respect to $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content. Final concentration of hydrogen peroxide after a 6-h reaction also showed a volcano-shaped curve with respect to $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content. Among the catalysts tested, CsPW/Pd/MCF-35.7 catalyst showed the best catalytic performance in terms of selectivity for hydrogen peroxide, yield for hydrogen peroxide, and final concentration of hydrogen peroxide. As mentioned earlier, it was observed that palladium dispersion on the catalysts was almost identical with no great difference. Therefore, it is believed that the difference in catalytic performance of CsPW/Pd/MCF- X catalysts was attributed to the variation of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ content.

In order to investigate the catalytic active site of CsPW/Pd/MCF- X ($X=10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts, CsPW/MCF-35.7 was employed for the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Conversion of hydrogen over CsPW/MCF-35.7 (1.3%) was significantly lower than that over CsPW/Pd/MCF-35.7 catalyst (81.2%). Selectivity for hydrogen peroxide over CsPW/MCF-35.7 (19.1%) was also lower than that over CsPW/Pd/MCF-35.7 catalyst (44.1%). As a consequence, yield for hydrogen peroxide over CsPW/MCF-35.7 (0.3%) was much lower than that over CsPW/Pd/MCF-35.7 catalyst (35.8%). Final concentration of hydrogen peroxide after a 6-h reaction over CsPW/MCF-35.7 (0.03 wt%) was also much lower than that over CsPW/Pd/MCF-35.7 catalyst (1.75 wt%). This result indicates that palladium of CsPW/Pd/MCF- X catalysts acted as an active site in the direct synthesis of hydrogen peroxide.

For comparison, Pd/MCF catalyst was applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Conversion of hydrogen over CsPW/Pd/MCF- X ($X=10.0, 21.7, 35.7, 52.6,$ and 68.9) catalysts (81.2–85.8%) was higher than that over Pd/MCF (76.4%). Selectivity for hydrogen peroxide over CsPW/Pd/MCF- X catalysts (34.7–44.1%) was much higher than that over Pd/MCF (1.6%). Consequently, yield for hydrogen peroxide over CsPW/Pd/MCF- X catalysts (28.8–35.8%) was much higher than that over Pd/MCF (1.2%). Final concentration of hydrogen peroxide after a 6-h reaction over CsPW/Pd/MCF- X catalysts (1.43–1.75 wt%) was also much higher than that over Pd/MCF (0.08 wt%). It has been reported that acid additives increase the selectivity for hydrogen peroxide by preventing the decomposition of hydrogen peroxide, because the dissociation of hydrogen peroxide ($\text{H}_2\text{O}_2 \rightleftharpoons \text{HO}_2^- + \text{H}^+$)

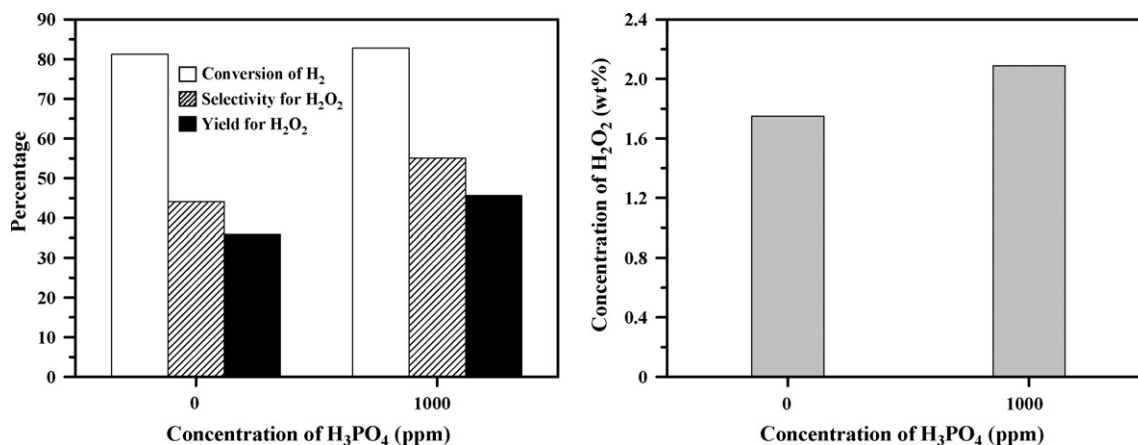


Fig. 7. Catalytic performance of CsPW/Pd/MCF-35.7 catalyst in the direct synthesis of hydrogen peroxide from hydrogen and oxygen after a 6-h reaction at different concentration of H₃PO₄.

is suppressed when hydrogen peroxide is surrounded by protons (H⁺ ions) of acid additives [1,22]. Therefore, it can be inferred that the improved selectivity for hydrogen peroxide over CsPW/Pd/MCF-X catalysts might be attributed to the enhanced acid property of CsPW/Pd/MCF-X catalysts.

3.3. Effect of additive on the catalytic performance

Fig. 7 shows the catalytic performance of CsPW/Pd/MCF-35.7 catalyst in the direct synthesis of hydrogen peroxide from hydrogen and oxygen at different concentration of H₃PO₄. 0.645 ml of 1 M H₃PO₄ solution was added to the reaction medium in order to make the concentration of H₃PO₄ become 1000 ppm. Conversion of hydrogen in the presence of H₃PO₄ was almost identical to that in the absence of H₃PO₄, while selectivity for hydrogen peroxide in the presence of H₃PO₄ was higher than that in the absence of H₃PO₄. Consequently, yield for hydrogen peroxide in the presence of H₃PO₄ was found to be higher than that in the absence of H₃PO₄. Final concentration of hydrogen peroxide in the presence of H₃PO₄ after a 6-h reaction was higher than that in the absence of H₃PO₄.

Fig. 8 shows the catalytic performance of Pd/MCF catalyst in the direct synthesis of hydrogen peroxide from hydrogen and oxygen at different concentration of H₃PO₄. In the absence of H₃PO₄, yield for hydrogen peroxide over Pd/MCF catalyst was very low, because selectivity for hydrogen peroxide over the catalyst was extremely low. Selectivity for hydrogen peroxide in the presence of H₃PO₄ was 10 times higher than that in the absence of H₃PO₄. This was

in good agreement with the fact that acid additives enhanced the selectivity for hydrogen peroxide by preventing the decomposition of hydrogen peroxide [1,22]. Yield for hydrogen peroxide in the presence of H₃PO₄ was much higher than that in the absence of H₃PO₄. Final concentration of hydrogen peroxide in the presence of H₃PO₄ after a 6-h reaction was also much higher than that in the absence of H₃PO₄. This indicates that formation of hydrogen peroxide over Pd/MCF catalyst was very sensitive to the amount of H₃PO₄ additive.

Direct comparison of Figs. 7 and 8 reveals that the catalytic performance of Pd/MCF catalyst was much more sensitive to the amount of H₃PO₄ additive than that of CsPW/Pd/MCF-35.7 catalyst. Furthermore, the catalytic performance of CsPW/Pd/MCF-35.7 catalyst even in the absence of H₃PO₄ was much higher than that of Pd/MCF catalyst in the presence of H₃PO₄. This result implies that Cs_{2.5}H_{0.5}PW₁₂O₄₀ served as an efficient and alternate acid source in the direct synthesis of hydrogen peroxide from hydrogen and oxygen.

Pd/MCF catalyst was also applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen in the presence of HBr instead of NaBr. One may expect that the catalytic performance of CsPW/Pd/MCF-X catalysts in the presence of NaBr will be similar to that of Pd/MCF catalyst in the presence of HBr, if HBr formed by an ion-exchange reaction between NaBr and Cs_{2.5}H_{0.5}PW₁₂O₄₀ only acts as an acid source in the direct synthesis of hydrogen peroxide. To clarify this, 0.078 ml of 1 M HBr solution was added to the reaction medium as a halide and an acid additive. Conversion

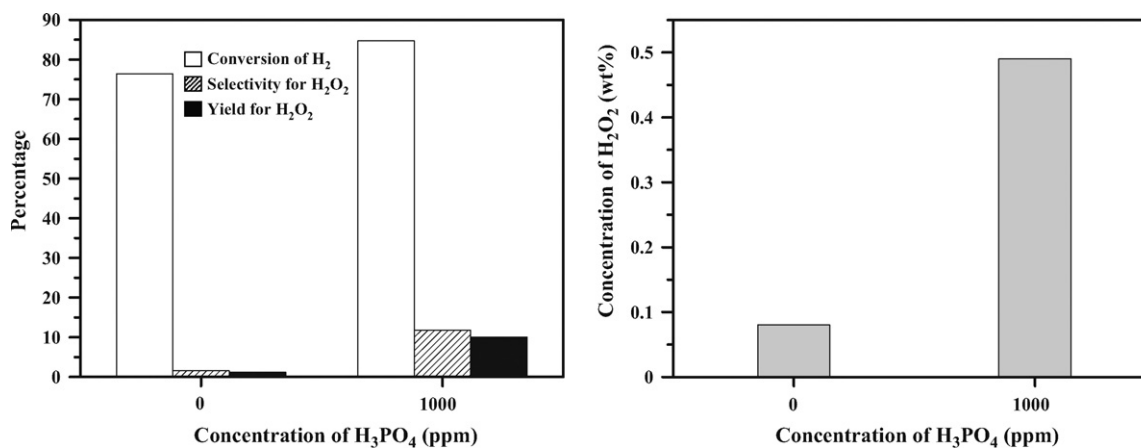


Fig. 8. Catalytic performance of Pd/MCF catalyst in the direct synthesis of hydrogen peroxide from hydrogen and oxygen after a 6-h reaction at different concentration of H₃PO₄.

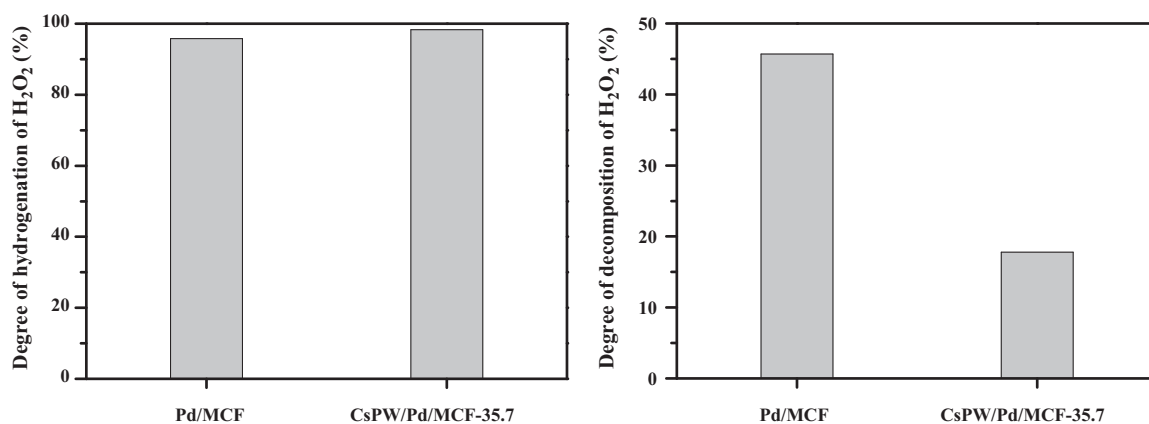


Fig. 9. Catalytic performance in the hydrogenation of hydrogen peroxide and the decomposition of hydrogen peroxide over Pd/MCF and CsPW/Pd/MCF-35.7.

of hydrogen and selectivity for hydrogen peroxide were 61.7 and 21.1%, respectively. As a consequence, yield for hydrogen peroxide was 13.0%. Final concentration of hydrogen peroxide after a 6-h reaction was 0.77 wt%. Selectivity for hydrogen peroxide and yield for hydrogen peroxide over Pd/MCF catalyst in the presence of HBr were much higher than those over the catalyst in the presence of NaBr. However, selectivity for hydrogen peroxide and yield for hydrogen peroxide over Pd/MCF catalyst in the presence of HBr were much lower than those over CsPW/Pd/MCF-*X* (*X* = 10.0, 21.7, 35.7, 52.6, and 68.9) catalysts in the presence of NaBr. Therefore, it is reasonable to conclude that Cs_{2.5}H_{0.5}PW₁₂O₄₀ of CsPW/Pd/MCF-*X* catalysts played an important role as a solid acid in the direct synthesis of hydrogen peroxide.

3.4. Catalytic performance in the hydrogenation of hydrogen peroxide and the decomposition of hydrogen peroxide

Fig. 9 shows the catalytic performance in the hydrogenation of hydrogen peroxide and the decomposition of hydrogen peroxide over Pd/MCF and CsPW/Pd/MCF-35.7. Both Pd/MCF and CsPW/Pd/MCF-35.7 showed high activity for hydrogenation of hydrogen peroxide. This indicates that the enhanced acid property of CsPW/Pd/MCF-35.7 catalyst showed no significant effect on the prevention of hydrogenation of hydrogen peroxide. On the other hand, activity for decomposition of hydrogen peroxide over CsPW/Pd/MCF-35.7 catalyst was much lower than that over Pd/MCF. This implies that the enhanced acid property of CsPW/Pd/MCF-35.7 catalyst inhibited the decomposition of hydrogen peroxide. Therefore, it can be said that CsPW/Pd/MCF-*X* (*X* = 10.0, 21.7, 35.7, 52.6, and 68.9) catalysts increased the selectivity for hydrogen peroxide by preventing the decomposition of hydrogen peroxide.

3.5. Acidity of Cs_{2.5}H_{0.5}PW₁₂O₄₀/Pd/MCF catalysts

Fig. 10 shows the NH₃-TPD profiles of Pd/MCF and CsPW/Pd/MCF-*X* (*X* = 10.0, 21.7, 35.7, 52.6, and 68.9) catalysts. Acidity of CsPW/Pd/MCF-*X* catalysts was measured from the peak area of the catalysts. Acidity of the catalysts is summarized in Table 1. It is interesting to note that acidity of the catalysts showed a volcano-shaped trend with respect to Cs_{2.5}H_{0.5}PW₁₂O₄₀ content. Among the CsPW/Pd/MCF-*X* catalysts, CsPW/Pd/MCF-35.7 showed the largest acidity. It has been reported that H₃PW₁₂O₄₀/SBA-15 with high H₃PW₁₂O₄₀ loading showed a relatively low acidity, because H₃PW₁₂O₄₀ formed aggregates on the pore walls and blocked the pore [36]. In this work, it was also observed that many aggregates of Cs_{2.5}H_{0.5}PW₁₂O₄₀ were out of the pore of Pd/MCF, as

shown in the TEM image of CsPW/Pd/MCF-52.6 catalyst (Fig. 11). This indicates that Cs_{2.5}H_{0.5}PW₁₂O₄₀ formed aggregates in the pore and blocked the pore of Pd/MCF. This result supports that acidity of CsPW/Pd/MCF-*X* decreased due to the restricted contact of ammonia (in the measurement of acidity) with Cs_{2.5}H_{0.5}PW₁₂O₄₀, when large amount of Cs_{2.5}H_{0.5}PW₁₂O₄₀ was loaded on Pd/MCF.

3.6. Effect of acidity on the catalytic performance

Experimental observations revealed that yield for hydrogen peroxide over CsPW/Pd/MCF-*X* (*X* = 10.0, 21.7, 35.7, 52.6, and 68.9) catalysts was closely related to the acidity of the catalysts, as shown in Fig. 12. Yield for hydrogen peroxide increased with increasing acidity of CsPW/Pd/MCF-*X* catalyst. Among the catalysts tested, CsPW/Pd/MCF-35.7 catalyst with the largest acidity showed the

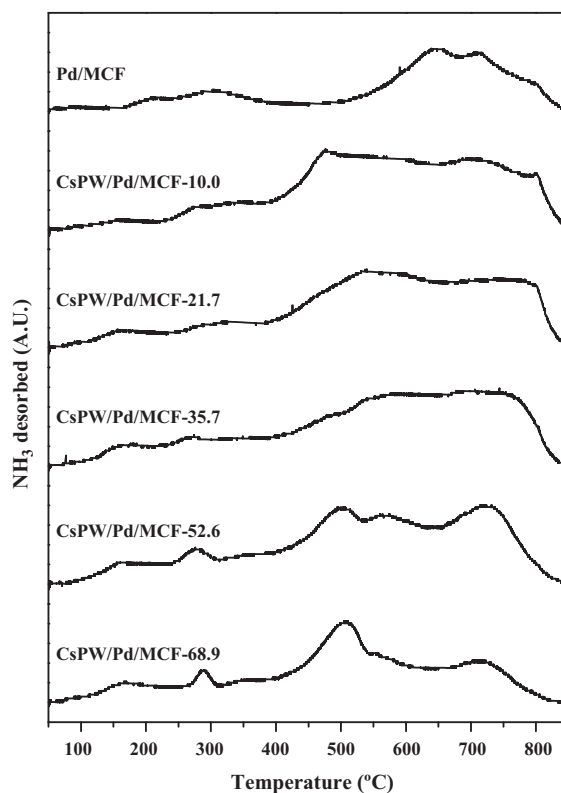


Fig. 10. NH₃-TPD profiles of Pd/MCF and CsPW/Pd/MCF-*X* (*X* = 10.0, 21.7, 35.7, 52.6, and 68.9) catalysts.

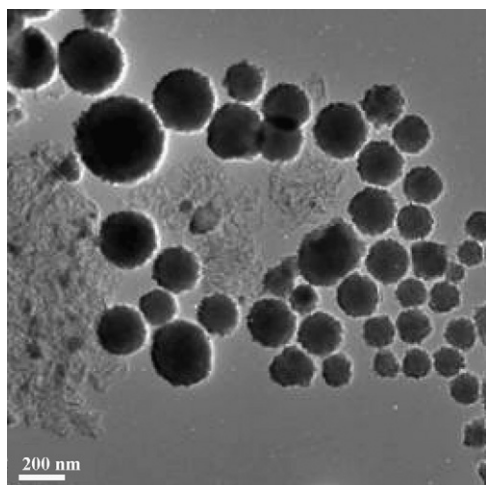


Fig. 11. TEM image of CsPW/Pd/MCF-52.6 catalyst (low magnification).

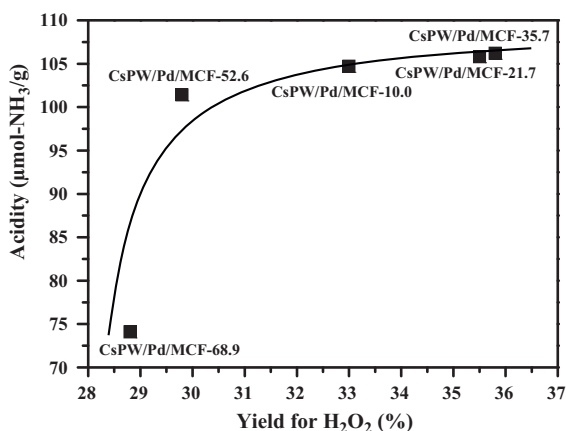


Fig. 12. A correlation between yield for hydrogen peroxide over CsPW/Pd/MCF-X (X=10.0, 21.7, 35.7, 52.6, and 68.9) catalysts and acidity of the catalysts.

highest yield for hydrogen peroxide. It has been reported that acidity on the catalyst surface is a crucial factor determining the catalytic performance in the direct synthesis of hydrogen peroxide, because protons prevent the decomposition of hydrogen peroxide by surrounding hydrogen peroxide [22]. Therefore, it is concluded that the improved yield for hydrogen peroxide over CsPW/Pd/MCF-35.7 catalyst was attributed to the enhanced acidity of the catalyst.

4. Conclusions

Insoluble Cs_{2.5}H_{0.5}PW₁₂O₄₀ heteropolyacid supported on Pd/MCF (CsPW/Pd/MCF-X (X=10.0, 21.7, 35.7, 52.6, and 68.9)) was prepared with a variation of Cs_{2.5}H_{0.5}PW₁₂O₄₀ content (X, wt%). The prepared catalyst was then applied to the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Selectivity for hydrogen peroxide, yield for hydrogen peroxide, and final concentration of hydrogen peroxide over CsPW/Pd/MCF-X catalysts showed a volcano-shaped curve with respect to Cs_{2.5}H_{0.5}PW₁₂O₄₀ content. Acidity of the catalysts also showed a volcano-shaped

trend with respect to Cs_{2.5}H_{0.5}PW₁₂O₄₀ content. It was revealed that yield for hydrogen peroxide increased with increasing acidity of CsPW/Pd/MCF-X catalyst. Among the catalysts tested, CsPW/Pd/MCF-35.7 catalyst with the largest acidity showed the highest yield for hydrogen peroxide. It is concluded that acidity of CsPW/Pd/MCF-X catalyst played an important role in determining the catalytic performance in the direct synthesis of hydrogen peroxide.

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