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Synthesis of Pd-M@HCS (M = Co, Ni, Cu) Bimetallic Catalysts and Their Catalytic Performance for Direct Synthesis of H₂O₂

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Abstract: Hydrogen peroxide (H₂O₂), as a clean and green oxidant, is widely used in many fields. The direct synthesis of H₂O₂ (DSHP) from H₂ and O₂ has attracted most research interest because it relates to a facile, environmentally friendly, and economic process. Yolk-shell Pd-M@HCS (hollow carbon sphere) (M = Co, Ni, Cu) nanocatalysts, in which the bimetal nanoparticle is the core and porous carbon works as the shell layer, are reported in this work. It was found that catalytic activities were enhanced because of the introduced M metals. Additionally, the different mass ratios of Pd to Co (mPd/mCo) were further investigated to improve the catalytic performance for the DSHP. When mPd/mCo was 4.4, the prepared Pd-Co@HCS-(4.4) catalyst, with an average Pd nanoparticle size of 7.30 nm, provided the highest H₂O₂ selectivity of 87% and H₂O₂ productivity of 1996 mmol g_{Pd}^{−1}·h^{−1}, which were increased by 24% and 253%, respectively, compared to Pd@HCS.

Keywords: direct synthesis of hydrogen peroxide; Pd-based catalyst; yolk-shell structure

1. Introduction

Hydrogen peroxide (H₂O₂), which has been diversely used for producing a wide range of products [1–6], is considered a green and clean raw material due to its highly atomic utilization and environmentally friendly properties. The direct synthesis of H₂O₂ (DSHP) from hydrogen and oxygen is believed a promising method since H₂O is the only by-product during the producing process [7–9]. However, the side reaction in the DSHP process, like the formation of H₂O, is more easily thermodynamic and thus results in a low selectivity of synthesis of H₂O₂ and a poor stability in general. To improve this process, palladium (Pd)-based catalysts as highly efficient active components have been extensively studied [10]. Moreover, bimetallic nanocatalyst have shown higher catalytic activity product selectivity and stability, thus attracting the most research interest. Recently, Pd-based bimetallic materials that were incorporated with 3d structure transition metals (such as Fe, Co, and Ni) were found to present excellent selectivity, stability and activity in various organic reactions [11]. Additionally, incorporating cheap transition metals can reduce the amount of the noble metal while maintaining decent catalytic activity. It was reported that a higher H₂O₂ yield was achieved by using Au-Pd/Al₂O₃ compared to Au/Al₂O₃ and Pd/Al₂O₃ in the DSHP process [12]. Simon et al. [13] proved that Pd-M/SiO₂ (M = Ni, Zn, Ga, In and Co) showed good catalytic activity in DSHP. However, the performance of such supported catalysts is still not desirable due to the migration, shedding, and agglomeration of the active component Pd. Recently, Violeta Paunovic et al. [14] reported

that an Au-Pd bimetallic catalyst in a wall-coated microchannel was developed for DSHP. The catalyst that is constructed on a microchannel wall can avoid migration, resulting in higher stability, selectivity, and productivity. However, the active sites might be covered by the microchannels and thus reduce the utilization of the catalyst. Inspired by these studies, this work developed bimetallic Pd-M (M = Co, Ni and Cu) catalysts with yolk-shell structures where the active component Pd-M was used as the core and a hollow carbon sphere was used as the shell (Pd-M@HCS). This yolk-shell structure can prevent the migration of the catalyst while enhancing the exposure of the active components of Pd-M to the reaction system. As a result, both the catalytic activity and atom utilization of the catalyst can be improved. This work provides a solution to the challenge that most of the active sites in conventional coated core-shell catalysts are covered with shell materials.

The Pd-M@HCS samples were synthesized by a reverse microemulsion method, where polyethylene glycol monocetyl ether (Brij56) was used as surfactant and cyclohexane and a Pd-M bimetallic nanosphere solution were used as the oil phase solvent and the aqueous phase, respectively. The formed water-in-oil reversed micelle was reduced by NaBH_4 to form Pd-M@HCS. Phenolic Resin(RF) nanospheres [15,16] and SiO_2 nanospheres [17] were synthesized by the polymerization of resorcinol, formaldehyde, and tetraethyl orthosilicate (TEOS), respectively. The TEM showed that the Pd was coated by the Co to form hollow nanospheres of Pd-Co@HCS. Thus, a suitable ratio of Pd to Co meant a better Pd-coated structure and led to a better catalytic performance. This work then further investigated the effect of different mass ratios of Pd to Co, $m_{\text{Pd}}/m_{\text{Co}}$, on the DSHP performance.

2. Results and Discussion

2.1. Characterization of Pd@HCS and Pd-M@HCS

2.1.1. Morphology of Pd@HCS and Pd-M@HCS

Figure 1 shows the morphology, histograms of the size distribution and element components of the prepared catalysts Pd@HCS and Pd-M@HCS (M = Co, Ni, Cu). The EDS patterns, shown in Figure 1a'''–d''', indicate that C, O, Si, Pd and Cu existed in all prepared samples. Pd, C and O were the main components of the catalysts. A small amount of Si was detected due to the unremoved SiO_2 during the etching process. The existing Cu was mainly from the copper grid for the TEM sampling. Additionally, the Co and Ni existing in the Pd-M@HCS (M = Co, Ni) indicated that the obtained catalysts were modified by Co and Ni. It should be noted that the intensity of Cu in Figure 1d''' is stronger than others, implying that the Cu was successfully incorporated into Pd-Cu@HCS.

As shown in Figure 1a–d, the TEM images revealed that the Pd and Pd-M nanoparticles were encapsulated with a carbon sphere, forming a multicore-shell structure where the metals were the cores and porous carbon was the shell layer. Additionally, the average particle size of the Pd nanoparticles in Pd@HCS among the prepared catalysts was the biggest with intensive agglomeration, as illustrated in Figure 1a'–d'. During the synthesis process, the cationic surfactant CTAB formed spherical micelles in which the hydrophobic hydrocarbon chains oriented inward, whereas the cationic hydrophilic groups directed outward. Because of electrostatic attraction, the $[\text{PdCl}_4]^{2-}$ (pH = 10) ions were mainly located on the surface of the spherical micelles, and M^{2+} ions were adsorbed on the $[\text{PdCl}_4]^{2-}$ ions. When CTAB was removed, the structure of the catalysts was assumed to be that of a hollow nanosphere. Nevertheless, the TEM images indicated that the composite contained several core crystals. The multi-core structure might have been formed during the pyrolysis process when the single crystal nanosphere was dispersed at a high temperature. Moreover, the free Pd atoms might have been deposited on the nanospheres when they were reduced by NaBH_4 and afterwards formed a multi-core structure as well. The formation of Pd-M@HCS is illustrated in Scheme 1. Scheme 1 shows the synthetic route for the yolk-shell nanocatalyst Pd@HCS. The core of the catalyst was Pd nanoparticles that were synthesized by a reverse microemulsion method, and the shell was a porous carbon sphere with a uniform thickness that was prepared by the calcination of a polymer resin layer, which was formed by the self-assembly of a cationic surfactant, CTAB, resorcinol, and RF. The preparation of the catalyst

Pd@HCS was divided into four steps. First is the synthesis of Pd nanoparticles, which was done with surfactant Brij56, co-surfactant n-octanol, the oil phase solvent cyclohexane, and an aqueous solution of Pd-M by a reverse microemulsion method. When the Pd-M solution was added dropwise into the oil-phase containing surfactant, it interacted more easily with the hydrophilic head of the surfactant due to the principle of dissolution in a similar material structure; then, it was surrounded by the oil phase solvent cyclohexane, and, in the end, a large number of water-in-oil nanodroplets were produced. These droplets served as nanoreactors that provided a unique environment for the nucleation and growth of the Pd nanoparticles. After the dynamic balance of the reverse microemulsion system was attained, the reductant NaBH₄ was added to this solution to reduce precursor Pd-M to Pd-M nanoparticles [18].

Figure 1. TEM images, histograms of the size distribution and EDS patterns of the catalysts: (a,a',a'',a''') Pd@HCS (hollow carbon sphere), (b,b',b'',b''') Pd-Co@HCS, (c,c',c'',c''') Pd-Ni@HCS and (d,d',d'',d''') Pd-Cu@HCS. (e–i) are EDS mapping analysis of Pd-Co@HCS.

Scheme 1. Synthetic route of Pd-M@HCS.

The growth of the Pd nanoparticles was inhibited when M components were introduced, resulting in a reduced particle size of metallic nanoparticles, as shown in Figure 1a'–d'. Additionally, after the removal of surfactant, the bimetallic crystal was nucleated, and the nanospheres were dispersed, thereby restricting the agglomeration of nanoparticles and further reducing the particle size.

Compared to Pd-Ni@HCS and Pd-Cu@HCS, Pd-Co@HCS presented the smallest average nanoparticle size (7.30 ± 0.67 nm), which was suggested to be more conducive to the DSHP reaction since the smaller size of the metal core could expose more active sites and thus enhance the dissociation of hydrogen bonds to generate H_2O_2 . The smaller size that existed in Pd-Co@HCS might have been caused by the smaller particle size of Co than that of Ni and Cu.

Figure 1e–i displays the EDS mapping of the Pd-Co@HCS, which illustrates that C, O, Si, Pd and Co were included in the prepared catalysts. This was consistent with the added elements during the preparation process. Moreover, due to the different reduction potentials of Co (II) and Pd (II), the metal that existed in the catalyst was a Pd-Co bimetal, not alloy. Their location was demonstrated in Figure 1h,i.

2.1.2. XRD Pattern of Pd@HCS and Pd-M@HCS

The XRD patterns of Pd@HCS and Pd-M@HCS, shown in Figure 2, demonstrate that the characteristic diffraction peaks of Pd, corresponding to Pd (1 1 1), (2 0 0) and (2 2 0), existed in the four prepared catalysts. Compared with Pd@HCS, the peaks of Pd in Pd-M@HCS shifted to higher 2θ , which clearly confirmed that the Pd-M bimetal catalysts [19] were obtained. The broad diffraction peak located at $2\theta = 25^\circ$ was attributed to amorphous carbon. In addition to the diffraction peaks of Pd existed in Pd-Co@HCS, the Co characteristic peak was not observed. It is assumed that the particle size of Co was too small to be detected by XRD. Furthermore, it can be suggested that the Pd-M bimetallic nanoparticles will react with SiO_2 to form a Pd-Si composite material [20] when carbonized at 600°C . In this work, the diffraction peaks of Pd_2Si were observed in Pd-Ni@HCS and Pd-Cu@HCS, and these were located at $2\theta = 41.3^\circ$ and 48.3° for Pd-Ni@HCS and $2\theta = 41.8^\circ$, 42.6° and 48.7° for Pd-Cu@HCS. Additionally, the existing Si in Pd-M@HCS helped to separate the bimetallic particles and thus limited the agglomeration of the core nanoparticles. As a result, multi-cores were generated. Additionally, the crystal sizes of Pd nanoparticles on Pd@HCS, Pd-Co@HCS, Pd-Ni@HCS and Pd-Cu@HCS that were calculated by the Scherrer formula were 13.55, 7.29, 8.40, and 8.52 nm, respectively, which were approximately consistent with the results from the TEM (Figure 1). The reduced size of the nanoparticles indicated that the agglomeration of Pd could be effectively reduced by incorporating the component M (Co, Ni and Cu).

Figure 2. XRD patterns of Pd@HCS and Pd-M@HCS.

2.1.3. N₂ Adsorption–Desorption of Pd@HCS and Pd-M@HCS

Figure 3a,b display the N₂ adsorption–desorption isotherms and pore size distribution (PSD) of the four catalysts, respectively. As shown in Figure 3a, all the four synthesized catalysts belonged a typical type II isotherm adsorption curve. The monolayer adsorption occurring at low relative pressure range ($P/P_0 < 0.01$) with a small amount of adsorbed N₂ indicated that all four catalysts contained micropores. The N₂ adsorption amount gradually increased with the increase of P/P_0 , but it increased sharply when $P/P_0 > 0.9$, indicating that all the four catalysts contained micropores and macropores. Moreover, a hysteresis loop appeared around P/P_0 from 0.4 to 0.9, which is a typical phenomenon of capillary agglomeration that occurs when N₂ is adsorbed simultaneously on mesopores and macropores. This reveals that the pores of the all the four catalysts were mainly composed of mesopores but contained some micropores and macropores. The different areas of the hysteresis loop of the four catalysts indicated that the mesoporous contents in the catalysts were different. For instance, the area of Pd@HCS was significantly larger than that of the other three catalysts, implying that it had the largest mesopore contents over others. As shown in Figure 3b, the pore size distribution of the four prepared catalysts was mainly located at 5–100 nm, which suggests that they had large numbers of mesopores and macropores with small amounts of micropores. The pores less than 2 nm were the pore channels of the porous carbon shell. The textural properties and Pd loading of the prepared samples is summarized in Table 1. It should be noted that the average micropore size of the porous carbon layer was larger than the kinetic diameters of the reactant molecules (H₂ and O₂), product molecule (H₂O₂) and by-product (H₂O), which facilitated mass transfer and diffusion when the catalysis reaction proceeded.

As listed in Table 1, the surface area (S_{BET}) and average pore volume (V_{mic}) were increased when M components were added. Pd-Co@HCS had the largest S_{BET} among them, which was beneficial for the diffusion of the reactants and products, resulting in an enhanced catalytic activity. The greater S_{BET} was also confirmed by TEM since the Pd-Co had a smaller nanoparticle size and better dispersion. On the other hand, the average shell pore size, D_{pore} , of Pd-Co@HCS was smaller than that of Pd-Ni@HCS and Pd-Cu@HCS, indicating that the Pd-Co nanoparticles could be easily encapsulated by the shell carbon and could consequently avoid agglomerating. Therefore, Pd-Co@HCS was assumed to be more efficient for the synthesis of H₂O₂. The Pd loading in the synthesized catalysts was around 4wt.%, as detected by ICP (Inductively Coupled Plasma) characterization; see Table 1.

Figure 3. N₂ adsorption–desorption of Pd@HCS and Pd-M@HCS. (a) Isotherm adsorption line; (b) pore size distribution.

Table 1. Textural properties and Pd loading of the prepared samples.

Catalysts	S _{BET} ^a (m ² /g)	V _{mic} ^b (cm ³ /g)	D _{pore} ^c (nm)	Pd Loading ^d (wt%)
Pd@HCS	379.01	0.09	15.83	4.05
Pd-Co@HCS	683.36	0.16	8.78	4.05
Pd-Ni@HCS	434.52	0.15	13.81	4.03
Pd-Cu@HCS	523.38	0.19	11.46	4.02

^a S_{BET} was calculated by the BET equation; ^b V_{mic} was calculated by the BJH equation; ^c D_{pore} was calculated by the density functional theory (DFT) model; ^d Pd loading was calculated by ICP characterization.

2.1.4. Activity Test of Pd@HCS and Pd-M@HCS for DSHP

Figure 4 shows the catalytic performances of the catalysts Pd@HCS and Pd-M@HCS for the direct synthesis of H₂O₂ from H₂ and O₂. Among them, Pd-Co@HCS provided the best H₂ conversion, H₂O₂ yield, H₂O₂ selectivity, and H₂O₂ productivity, which were 33%, 29%, 87% and 1996 mmolg_{Pd}^{−1}h^{−1}, respectively. Compared with Pd@HCS (10%, 7%, 70% and 565 mmolg_{Pd}^{−1}h^{−1}), the H₂ conversion, H₂O₂ yield, H₂O₂ selectivity, and H₂O₂ productivity were increased by 230%, 314%, 24%, and 253%, respectively. As discussed before, the larger number of high-energy active sites that were exposed on Pd-Co than Pd due to the smaller core size was more conducive to the DSHP reaction. Meanwhile, Pd-Co@HCS had a larger specific surface area and pore volume, which could provide stronger adsorption of H₂ and O₂, thereby improving the catalytic selectivity. Additionally, the H₂ conversion was improved because the highly dispersed Pd-Co surface provided a higher concentration of active hydrogen by diffusing hydrogen from Pd to Co. In addition, the enhanced catalytic performances of Pd-Co@HCS was also attributed to synergistic effect between Pd and Co, as well as the bi-site effect where both metals played specific role with respect to the reactants [21]. Since Pd-Co@HCS presented an attractive catalytic performance for the DSHP, the different mass ratios of Pd to Co were investigated further.

2.2. Characterization of Pd-Co@HCS-(X)

2.2.1. XRD pattern of Pd-Co@HCS-(X)

Figure 5 shows the XRD patterns of Pd-Co@HCS-(1), Pd-Co@HCS-(2.8), Pd-Co@HCS-(4.4) and Pd-Co@HCS-(6.6). Diffraction peaks of Pd (1 1 1), (2 0 0) and (2 2 0) at 2θ = 40.1°, 46.7° and 68.1°, respectively, were observed. The abroad perk located at 2θ = 25° was amorphous carbon. Except for the characteristic diffraction peaks of Pd and carbon, no new diffraction peak was detected for the four catalysts. It was assumed that the particle size of Co was very small and thereby lower than the detection limitation of XRD. The crystal sizes of Pd, calculated by the Scherrer formula, were 9.33 nm (Pd-Co@HCS-(1)), 8.82 nm (Pd-Co@HCS-(2.8)), 7.29 nm (Pd-Co@HCS-(4.4)), and 8.94 nm (Pd-Co@HCS-(6.6)). As the mass ratio m_{Pd}/m_{Co} increased from 1 to 4.4, the Pd crystal sizes decreased

from 9.33 to 7.29 nm. The exposed active sites from Pd were increased when Co amount reduced (namely higher $m_{\text{Pd}}/m_{\text{Co}}$ value) since Co might have covered certain Pd active sites. When the $m_{\text{Pd}}/m_{\text{Co}}$ increased to 6.6, however, the crystal size increased to 8.94 nm, which can be explained by fact that the agglomeration of the Pd nanoparticles occurred due to a small amount of Co being insignificantly dispersed in the Pd. Therefore, a proper ratio between Pd and Co (4.4:1) can provide more catalytic active sites from Pd and improve the dispersion of Pd, simultaneously.

Figure 4. Catalytic activity of the prepared catalysts Pd@HCS and Pd-M@HCS. (a) H_2 conversion, (b) H_2O_2 yield, (c) H_2O_2 selectivity, and (d) H_2O_2 productivity.

Figure 5. XRD patterns of Pd-Co@HCS(X).

2.2.2. N₂ Adsorption–Desorption of Pd-Co@HCS-(X)

Figure 6 shows N₂ adsorption–desorption isotherms and pore size distribution of Pd-Co@HCS. Similarly, all the synthesized catalysts presented a typical type II isotherm adsorption curve. The monolayer adsorption at low relative pressure range ($P/P_0 < 0.01$) indicated that all the Pd-Co@HCS-(X) samples contained micropores. The adsorbed N₂ gradually increased with the increase of P/P_0 , while it sharply increased when $P/P_0 > 0.9$, indicating that both micropores and macropores existed in Pd-Co@HCS-(X). Meanwhile, the hysteresis loops revealed that the Pd-Co@HCS-(X) catalysts were mainly composed of mesopores. The PSD shown in Figure 6b also illustrates that they had small numbers of micropores with pore sizes of 1–2 nm and large numbers of mesopores and macropores. The S_{BET} , V_{mic} and D_{pore} are summarized in Table 2. As mentioned before, a higher specific surface area can enhance H₂O₂ selectivity by providing more adsorption sites for H₂ and O₂ molecules. Thus, Pd-Co@HCS-(4.4), with the highest $S_{\text{BET}} = 683.36 \text{ m}^2/\text{g}$, probably has the best catalytic performance for DSHP.

Figure 6. N₂ adsorption–desorption of Pd@HCS-(X). (a) Isotherm adsorption line; (b) pore size distribution.

Table 2. Textural properties and Pd loading of Pd-Co@HCS-(X).

Catalysts	S_{BET} (m ² /g)	V_{mic} (cm ³ /g)	D_{pore} (nm)	Pd Loading (wt%)
Pd-Co@HCS-(1)	487.96	0.17	12.29	4.05
Pd-Co@HCS-(2.8)	601.61	0.19	9.97	4.05
Pd-Co@HCS-(4.4)	683.36	0.16	8.78	4.05
Pd-Co@HCS-(6.6)	400.03	0.13	14.99	4.05

2.2.3. Activity Test of Pd-Co@HCS-(X) for DSHP

Figure 7 demonstrates the effect of the ratio of $m_{\text{Pd}}/m_{\text{Co}}$ on the catalytic performances for the direct synthesis of H₂O₂ from H₂ and O₂. As expected, Pd-Co@HCS-(4.4) had the largest surface area and provided the best H₂O₂ selectivity of 87% and H₂O₂ productivity of $1996 \text{ mmol}_{\text{Pd}}^{-1} \cdot \text{h}^{-1}$.

Figure 7. Catalytic activity of Pd-Co@HCS-X ($X = 1, 2.8, 4.4$ and 6.6). (a) H_2 conversion, (b) H_2O_2 yield, (c) H_2O_2 selectivity, and (d) H_2O_2 productivity.

3. Experimental

3.1. Materials

Chloropalladic acid (H_2PdCl_4 , AR) was purchased from Sigma-Aldrich (Shanghai, China). Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, AR), nickel chloride ($NiCl_2 \cdot 6H_2O$, AR), copper chloride ($CuCl_2 \cdot 2H_2O$), hydrofluoric acid (HF, 40%, AR), and sodium borohydride ($NaBH_4$, 96%, AR) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Cyclohexane, *n*-octanol, absolute ethanol (99.7%, AR) and methanol (99.5%, AR) were purchased from Tianjin Fuyu Fine Chemical Co. (Shanghai, China). Tetraethyl orthosilicate (TEOS, 9.0%, AR) was purchased from Aladdin (Shanghai, China). Cetyltrimethylammonium bromide (CTAB, 99.0%, AR) and Brij56 were purchased from Tokyo Chemical Industry (Shanghai, China). Ethylene glycol (AR), ammonia solution (25%–28%, AR), resorcinol (99.5%, AR), and H_2O_2 (30%, AR) were purchased from Chengdu Jinshan Chemical Reagent Co., Ltd. (Shanghai, China). Sulfuric acid (H_2SO_4 , 98%, AR) was purchased from Tianjin Chemical Reagent Factory Kaida Chemical Factory (Shanghai, China). Formaldehyde (37.0%–40.0%, AR) was purchased from Xilong Science Co., Ltd (Shanghai, China).

3.2. Catalyst Preparation

Zero-point-zero-eight grams of CTAB were dissolved in 10 mL of ethylene glycol and then mixed with a 0.075 M precursor aqueous solution (H_2PdCl_4 , $Co(NO_3)_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$). The pH was adjusted to 10 by adding an ammonia aqueous solution. The Pd-M seed solutions were then formed after reacting for 2 h.

Eight-point-seven-two grams of the Brij56 surfactant were added into a mixed solution of 40 mL of cyclohexane and 10 mL of *n*-octanol at 35 °C with magnetic stirring to a form homogeneous solution. Afterward, the Pd-M seed solution was added and stirred for 2 h. Then, 450 µL of a 10 wt.% NaBH₄ solution was dropped in (the color of the solution changed to black), and after 30 min, 2 mL of an ammonia aqueous solution was added into to the black solution. Two milliliters of TEOS was added after 1 h, and the hydrolytic condensation reaction of the silica precursor was proceeded for 6 h. Afterward, the microemulsion was damaged by adding 50 mL of ethanol. Finally, Pd-M@SiO₂ was obtained by centrifugation and was washed with ethanol three times.

The as-obtained Pd@SiO₂ was dispersed in a mixed solution of 70 mL of deionized water and 30 mL of ethanol by ultrasonication, followed by the addition of 4 g of CTAB with magnetic stirring at 35 °C for 30 min; 0.35 g resorcinol was then added to the solution. After the resorcinol was dissolved, 0.5 mL of formaldehyde and 0.2 mL of an ammonia solution were added to the solution under stirring and then stirred for 6 h to form a uniform dispersion. The mixture was centrifugated and washed with ethanol three times. Afterward, the product Pd-M@SiO₂@RF was collected after being dried at 50 °C for overnight.

The obtained Pd-M@SiO₂@RF was pyrolyzed at 600 °C for 2 h under an N₂ atmosphere to remove CTAB and to form Pd-M@SiO₂@C. Next, Pd-M@SiO₂@C was dispersed in 36 mL of deionized water, and then the mixture was etched by adding 5 mL of an HF solution. After being stirred for 12 h, the product was centrifugated and washed by DI water 3 times and then dried at 80 °C overnight to obtain Pd-M@HCS. Finally, the catalyst for DSHP was collected by calcined under air for 2 h and then reduced at 250 °C under H₂ for 2.5 h. The prepared Pd-Co@HCS with different mass ratios of m_{Pd}:m_{Co} = 1:1, 2.8:1, 4.4:1 and 6.6:1 were referred as Pd-Co@HCS-(1), Pd-Co@HCS-(2.8), Pd-Co@HCS-(4.4) and Pd-Co@HCS-(6.6), respectively.

3.3. Catalyst Characterization

The morphology, size, and elemental composition of the catalyst were determined by a Tecnai G2 F20 S-Twin TEM (transmission electron microscope) that was equipped with an energy-dispersive X-ray (EDX) spectroscopic analyzer (city, State Abbr. (if has), country) and operated at a voltage of 200 kV. The XRD patterns were obtained by using a D8 Advance diffractometer (city, State Abbr. (if has), country) that operated at 40 kV and 40 mA with Cu Kα radiation (λ = 1.5418 Å). The surface areas and pore structures were measured by using an ASAP 2020 M analyzer (Micromeritics Co.) at 77 K.

3.4. Activity Test

The catalytic performance of the catalysts for the DSHP reaction was tested for 1 h in a jacketed glass reactor at 0 °C and 0.1 MPa. A mixed solution of 80 mL of methanol (99.7%) and 0.9 mL of H₂SO₄ (98%) was used as the reaction medium. The total flow rate of the reactants was kept at 16 mL/min, including 2 mL/min H₂, 4 mL/min O₂, and 10 mL/min N₂. The concentration of the generated H₂O₂ and remaining H₂ were detected by iodometric titration and gas chromatography, respectively. H₂ conversion, H₂O₂ selectivity, H₂O₂ yield, and H₂O₂ productivity were calculated by the following equations:

$$\text{H}_2 \text{ conversion (\%)} = \frac{\text{moles of H}_2 \text{ reacted}}{\text{moles of H}_2 \text{ fed}} \times 100$$

$$\text{H}_2\text{O}_2 \text{ yield (\%)} = \frac{\text{moles of H}_2\text{O}_2 \text{ formed}}{\text{moles of H}_2 \text{ fed}} \times 100$$

$$\text{H}_2\text{O}_2 \text{ selectivity (\%)} = \frac{\text{moles of H}_2\text{O}_2 \text{ formed}}{\text{moles of H}_2 \text{ reacted}} \times 100$$

$$\text{H}_2\text{O}_2 \text{ productivity (mmol g}_{\text{Pd}}^{-1} \cdot \text{h}^{-1}) = \frac{\text{moles of H}_2\text{O}_2 \text{ formed}}{\text{mass of Pd fed} \times \text{time}}$$

4. Conclusions

The yolk-shell structure nanocatalyst Pd-M@HCS (M = Co, Ni, Cu) with bimetal nanoparticles as its core and porous carbon as its shell layer was successfully synthesized by reverse micelle and self-assembly methods. The incorporated M components enhanced H₂O₂ selectivity and H₂O₂ productivity by reducing the Pd nanoparticle crystal size and forming more active sites. Pd-Co@HCS provided the best catalytic performances for DSHP with an H₂ conversion of 33%, an H₂O₂ yield of 29%, an H₂O₂ selectivity of 87%, and an H₂O₂ productivity of 1996 mmol_{Pd}⁻¹·h⁻¹, and these were increased by 230%, 314%, 24%, and 253%, respectively, compared to Pd@HCS. Furthermore, the effect of Co content in the Pd-Co on the catalytic activities was investigated. It was found that the catalyst showed the best performance when the ratio m_{Pd}:m_{Co} was 4.4:1. This was because when the mass ratio m_{Pd}/m_{Co} increased from 1 to 4.4, the Pd crystal sizes decreased from 9.33 to 7.29 nm. Meanwhile, the more Pd active sites were exposed when m_{Pd}/m_{Co} = 4.4. However, when the m_{Pd}/m_{Co} increased to 6.6, the crystal size increased to 8.94 nm because of the agglomeration of the Pd nanoparticles. Therefore, a proper mass ratio between Pd and Co can provide more efficient catalytic activity. What is more, the yolk-shell structure nanocatalyst Pd-M@HCS (M = Co, Ni, Cu) with bimetal nanoparticles as its core and porous carbon as its shell layer can also be applied to electrocatalysis [22,23].

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