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Reducing Agent-Structure-Activity Relationship of PdAg/C Catalysts in Formic Acid Decomposition for Hydrogen Generation

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The reducing agent effect on surface structure and then catalytic activity towards formic acid decomposition for hydrogen generation of PdAg/C nanoparticles was investigated. The PdAg/C catalysts were prepared by four different reducing agents including formic acid, hydrogen, sodium borohydride and ascorbic acid. X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy were used to evaluate the physical structure of PdAg nanoparticles. It was found that reducing agents affected degree of alloying, particle size, atoms distribution and electronic state of the PdAg surface. The combination of structure with activity results indicated that the abundant and electron-rich Pd atoms benefited the catalytic activity. The PdAg/C catalyst prepared by using formic acid as a reducing agent showed high selectivity, high durability and the highest initial turnover frequency of 90 h⁻¹ for hydrogen generation from formic acid decomposition without any additive at room temperature.

Keywords: Formic Acid Decomposition, PdAg, Reducing Agent.

1. INTRODUCTION

Hydrogen generation from formic acid (FA) decomposition has attracted extensive research interests due to advantages including bio-renewability, non-toxicity, high energy density and high stability at room temperature of FA. It is known that the active heterogeneous catalysts towards FA decomposition are noble metals such as Pd,^{1–3} Pt^{4, 5} and Au.^{6–8} Among these metals, Pd has been thought to possess more interesting catalytic performance. Then, much attention has been paid to develop bi/tri-metallic Pdbased composite catalysts in order to improve the dehydrogenation performance of FA.^{9–19} The enhancement was attributed to factors such as changed Pd–Pd interatomic distance, modified electron state, modified morphology and distribution of metal atoms on the catalyst surface.

One interesting second metal is Ag, which shows a similar lattice constant with Pd and a low price of only about 3 percent of Pd. Tedsree et al.¹⁵ constructed well-defined Pd@Ag core–shell bimetal nanoparticles by using polyvinylpyrrolidone as a stabilizer and reported that the

Pd shell containing 1-2 layers of atoms could be electronically promoted by the Ag core, leading to significantly enhanced catalytic properties towards FA decomposition. Zhang and co-workers¹⁶ synthesized 2.2 nm monodisperse Pd₅₈Ag₄₂ alloy nanoparticles by using oleylamine as a reducing agent, which were supported onto carbon and showed a high initial TOF of 382 h⁻¹ at 50 °C towards FA without any additive. In another research, agglomerated PdAg bimetal nanoparticles were simply prepared by using sodium borohydride (SB) as a reducing agent. The unsupported PdAg nanoparticles were reported to benefit the separation of catalysts from the liquid system to control the FA decomposition at any moment.¹⁷ Recently, Jiang et al.¹⁸ reported a simple wet-chemical method for the synthesis of PdAg hollow spheres anchored on graphene. The hollow architecture with thin outer shells contributed to high surface area of catalytic active sites and then showed a high initial TOF of 333 h⁻¹ at room temperature towards the mixture solution of FA and sodium formate.

Obviously, the catalytic activity of PdAg bimetal catalyst depends greatly on their preparation methods and structures. It is significant to explore the structure-activity

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relationship of PdAg for the development of highperformance Pd-based catalysts towards FA decomposition. For bimetal nanoparticles, synthetic reducing agent has been demonstrated to play a key role in the final bimetal structure.²⁰⁻²⁴ The surface compositions, morphologies and degrees of alloying of bimetal will be influenced due to different reduction rates of two metal precursors. In this study, the effect of reducing agents on PdAg structure and then catalytic activity towards FA decomposition was examined. The surface-clean PdAg/C catalysts were prepared by a traditional impregnationreduction method with different reducing agents including SB, FA, ascorbic acid (AA) and hydrogen. The combined results of structure with catalytic activity indicated that both the abundant Pd atoms and electron-rich state of Pd atoms in the catalyst surface benefited the catalytic performance towards FA decomposition. For example, the highest activity was observed in the PdAg/C nanoparticles prepared from FA and attributed to abundant Pd atoms in the catalyst surface.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

All PdAg/C catalysts were prepared by a conventional impregnation-reduction method. The PdAg/C catalyst from the use of SB as a reducing agent was synthesized as follows. For the first step, 140 mg of Vulcan XC-72 carbon powder was ultrasonically dispersed in 400 mL of water and subsequently mixed with 2×10^{-4} mol Pd(NO₃), and 2×10^{-4} mol AgNO₃. Then, freshly prepared 20 mL of 100 mM SB aqueous solution was dropped into the above suspension. The mixture was stirred for another 8 h at room temperature in order to deposit the bimetal particles onto the support absolutely. Finally, the desired catalyst (referred to as PdAg/C-SB) from the suspension was filtered and washed with water and then dried in vacuum at 80 °C overnight. The PdAg/C catalysts from the use of FA and AA as reducing agents were also synthesized by the same wet-reduction method except that FA/sodium formate (1:1) and AA were used, and referred to as PdAg/C-FA and PdAg/C-AA, respectively. Another PdAg/C catalyst with hydrogen used as a reducing agent was also prepared by a gas-reduction method and referred to as PdAg/C-H. 140 mg of Vulcan XC-72 carbon powder, 2×10^{-4} mol Pd(NO₃)₂ and 2×10^{-4} mol AgNO₃ were added into 10 mL of water. The mixture was stirred at 60 °C until the solvent was volatilized and then dried at 60 °C overnight. The obtained dry powder was ground and treated by a hydrogen flow at 60 °C for 2 h in a tube furnace. Finally, the black powder was filtered and washed with water and then dried in vacuum at 80 °C overnight. For comparison, the monometallic catalysts of Pd/C and Ag/C were also prepared separately by using the same wet-reduction method and FA as reducing agent.

2.2. Physical Characterizations

X-ray diffraction (XRD, Bruker D8-Focus, Germany) measurements were carried out with a scanning speed of 2 degree min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were done by using a Kratos XSAM-800 spectrometer with an Mg K α radiator. Transmission electron microscopy (TEM) was performed by using a FEI Titan G² 60-300 Probe Cs Corrector HRSTEM system. Fourier-transform infrared spectroscopy (FT-IR, PerkinElmer Nicolet6700, USA) was used for CO determination. During the FT-IR analysis, a cylindrical vessel with a volume of about 150 mL was used. Firstly, the vessel was vacuumed by using a pump. Then, the gas for detection was injected into the vessel by using an injector until the vessel was full of the gas at an atmospheric pressure. Finally, FT-IR spectra of the gas were recorded with a scan resolution of 2 cm $^{-1}$. 32 cycles were made before results came out. N2 was used for blank measurement.

2.3. Measure the Activity of the Catalysts for FA Decomposition

The FA decomposition reaction was performed in a test tube containing 5 mL of 1 M FA at 25 °C under ambient atmosphere. The reforming gases from this reaction were measured by using a gas burette. In order to check activation energy of the catalysis reaction, the reaction was also checked at 45, 60 and 80 °C, respectively.

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3. RESULTS AND DISCUSSION

The XRD patterns of the prepared catalysts were shown in Figure 1. For all the catalysts, the broad peaks between 20° to 30° were from graphite structure of carbon while the other peaks were from face centered-cubic phase of metals. For example, the 2θ values of 38.1° and 44.3° in Figure 2(a) were indexed to diffraction of (111) and (200)



Figure 1. XRD patterns of (a) Ag/C, (b) Pd/C, (c) PdAg/C–SB, (d) PdAg/C–H, (e) PdAg/C–FA after three run of catalysis reaction, (f) PdAg/C–FA and (g) PdAg/C–AA.

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Figure 2. TEM images of (a) PdAg/C–SB, (b) PdAg/C–AA, (c) PdAg/C–FA and (d) PdAg/C–H.

planes of Ag, respectively. For all the PdAg/C catalysts, there existed diffraction peaks in the position between the corresponding Ag and Pd peaks, indicating that the formation of PdAg alloy in the catalyst. In addition, a weak shoulder peak at the position of Pd diffraction could also be observed in the XRD pattern of the PdAg/C-H and indicated some unalloyed Pd crystals in the samples. According to the diffraction peaks of PdAg alloy (111), the average crystallite sizes were calculated to be 5.3, 6.6, and 7.0 nm for PdAg/C-SB, PdAg/C-FA, and PdAg/C-AA in sequence. Figure 2 shows the TEM images of PdAg/C catalysts synthesized by different reducing agents. For all the catalysts, PdAg nanoparticles (black dots) were wellsupported on the carbon (the gray base). The average particle sizes of the catalysts were given in Table I. The PdAg nanoparticles from wet-chemical reduction method were found to have comparable average particle size of about 5 nm while those from gas-chemical reduction method have a larger average particle size with apparent particle aggregation. These results agreed with the calculated average crystal size from the above XRD results.

XPS measurements were carried out to determine both the compositions and electronic properties of the

as-prepared catalysts. The calculated molar ratios of Pd to Ag were shown in Table I. The obtained Pd/Ag molar ratios from XPS results were found to be higher than those from the precursors for the PdAg/C-AA, PdAg/C-FA, and PdAg/C-H catalysts. This result meant the Pd atoms trended to form in the surface of PdAg catalysts during the preparation. For the same reason, one could conclude that Ag atoms trended to form in the surface of the PdAg bimetal when SB was used as reducing agent, which was also observed in the preparation of unsupported PdAg nanoparticles by using the same reducing agent.¹⁵ As shown in Figure 3, the binding energies of Pd 3d in PdAg/C-FA shifted to higher values compared to those in Pd/C, while the binding energy of Ag 3d in PdAg/C-FA shifted to lower values compared to those in Ag/C. This result demonstrated that some electrons were transferred from the Pd to Ag atoms. This phenomenon was also observed in the preparation of reported porous PdAg nanoalloy catalyst.¹⁹ It was reported that the Pd/C prepared by using AA as a reducing agent showed lower binding energy of Pd than that by using SB.²⁵ However, the results shown in Table I indicated that AA brought out higher and lower binding energy of Pd 3d and Ag 3d compared to SB, respectively. This phenomenon might relate to the different reducing potential between Pd and Ag precursors in the preparation of PdAg bimetal nanoparticles. Then, the influences of reducing agents on the electronic properties of PdAg bimetal were more complicated than that of monometal and implied the opportunities to tune bimetal electronic properties by optimizing reducing agents.

The catalytic activity of all the prepared catalysts was tested by collecting the generated gas from the decomposition of FA without any additive at room temperature. The Ag/C seemed inactive because no gas or bubble was observed while the Pd/C was distinctly active. The inactive Ag catalysts towards FA decomposition have also been reported by others.^{11, 16, 26} Then, the active sites of PdAg bimetal might be Pd rather than Ag towards the catalysis reaction in this study. As shown in Figure 4, the catalytic activity was distinct from the prepared different PdAg catalysts. All the PdAg catalysts showed higher activity than Pd/C catalyst except PdAg/C–AA. Then, it was feasible to increase the catalyst performance of Pd by introducing Ag into Pd with a suitable reducing agent.

The activity-structure relationship was discussed by combining the above physical characterization with

Table I. The Pd/Ag molar ratio, binding energy of Pd and Ag of the prepared catalysts.

Catalyst	PdAg/C-FA	PdAg/C-SB	PdAg/C-H	PdAg/C-AA	Pd/C	Ag/C
Pd/Ag from XPS	2.34	0.81	2.48	2.97	_	_
Pd/Ag from precursors	1	1	1	1	_	_
Binding energy of Pd $3d_{5/2}$ (eV)	335.53	335.83	335.52	337.26	335.33	_
Binding energy of Ag $3d_{5/2}$ (eV)	367.89	368.06	367.86	367.79	_	368.27
Crystal size from XRD (nm)	6.6	5.3	_	7.0	_	_
Particle size from TEM (nm)	5.0	4.8	7.5	5.3	-	-

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Figure 3. XPS spectra of (a) Ag 3d and Pd 3d (b) of corresponding Ag/C, AgPd/C and Pd/C catalysts.

activity results. PdAg/C-AA showed the highest Pd/Ag molar ratio in the catalyst surface, which indicated more active sites of Pd for the catalysis reaction. However, its catalytic activity was the lowest among these four PdAg/C catalysts and indicated low specific activity of Pd atoms in PdAg/C-AA. This might be related to the poor-electron state of Pd in PdAg/C-AA, which could be observed from the highest binding energy of Pd 3d. In many research, electron has been considered to benefit the catalytic activity of Pd towards FA decomposition.^{14,27} Among the other three PdAg/C catalysts, the observation of the lowest activity in PdAg/C-SB was reasonable because it showed the highest binding energy and lowest Pd/Ag molar ratio in the catalyst surface. In addition, the PdAg/C-FA showed close binding energy and Pd/Ag molar ratio to the PdAg/C-H. However, the catalytic activity of PdAg/C-FA was higher than that of PdAg/C-H. The poor alloy state, relatively large particle size and bad dispersion of nanoparticles in PdAg/C-H might be the reason. Therefore, the PdAg bimetal surface with abundant Pd atoms, electron-rich and



Figure 4. Volume change of reforming gas with time for 50 mg of the synthesized catalyst in 5 ml of 5 M formic acid aqueous solution at 25 °C.

alloyed state might benefit the catalytic activity toward FA decomposition, which could be tuned by choosing suitable reducing agents during the preparation.

Among all the prepared catalysts, PdAg/C-FA displayed the highest catalytic performance and showed an initial TOF of 90 h^{-1} , which was comparable with those of reported active Pd based catalysts towards FA decomposition without any additive.^{14, 19, 28} The activation energy was also evaluated by controlling the temperature of decomposition reaction on the PdAg/C-FA catalyst. It was determined to be as low as 29.6 kJ mol⁻¹ and indicated the active property of the PdAg nanoparticles. The recycle test of the prepared PdAg/C-FA catalyst was also carried out for the same decomposition reaction and the results were shown in Figure 5. There was almost no deactivation after three runs of catalysis reactions. The XRD pattern of the catalyst after three runs of catalysis reactions was shown in Figure 1 and found to be very close to the as-prepared fresh catalyst. These results denoted the good



Figure 5. Durability test for the dehydrogenation of FA over PdAg/C–FA catalyst at 25 °C.

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Figure 6. FT-IR spectra for CO detection: (a) 100 ppm CO, (b) 75 ppm CO, (c) 50 ppm CO, (d) 30 ppm CO and (e) the reforming gas from the FA decomposition on PdAg/C–FA catalyst at 25 °C.

stability of the PdAg/C catalyst during the FA decomposition. The CO content of the reforming gas from FA decomposition on the PdAg/C–FA catalyst was examined by FT-IR. As shown in Figure 6, there was no observation of characteristic adsorption peaks of CO between 2040 and 2200 cm⁻¹. This result indicated high selectivity of decomposition pathway and high quality of reforming gases, which was always a favor in fuel cell applications.

4. CONCLUSIONS

The structure-activity relationship of PdAg/C catalysts was studied by tuning the reducing agents during the preparation. It was found that the reducing agents influenced the degree of alloying, particle size, atoms distribution and electronic state of the PdAg surface. For example, all the reducing agents except SB promoted the formation of Pd in the PdAg surface. The particle sizes of PdAg nanoparticles from the gas-reduction method were larger than those from the wet-reduction method. The weak reducing agent of AA produced electron-rich Ag atoms and electronpoor Pd atoms. The combination of PdAg nanoparticle structure with activity results indicated that the abundant and electron-rich Pd atoms in the PdAg bimetal surface benefited the catalytic activity, which could be possibly designed by selecting a suitable reducing agent. The best PdAg/C catalyst was prepared from FA and showed high activity, selectivity and durability for hydrogen generation from FA decomposition without any additive at room temperature.

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