Supplemental Information for

Highly Efficient Dehydrogenation of Formic Acid over Binary Palladium-Phosphorous Alloy Nanoclusters on N-Doped Carbon

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Experimental

Chemicals and Materials

Palladium (II) chloride (PdCl₂, 99.9 wt. %), sodium hypophosphite (NaH₂PO₂), sodium borohydride (NaBH₄), commercial palladium nanoparticles (Pd NPs), Vulcan XC-72 were obtained from Sigma-Aldrich. To prepare 10 mM H₂PdCl₄ solution, 0.355 g of PdCl₂ was first dissolved into 20 mL of 0.2 M HCl solution, and then diluted with 180 mL of deionized H₂O. Deionized H₂O with the resistivity of 18.25 m Ω was used in all experiments.

Synthesis of N-doped Vulcan XC-72 (NC)

Nitrogen doped Vulcan XC-72 (BC) was synthesized according to previous report.¹

Synthesis of PdP/NC and Pd/NC

PdP/NC was synthesized by an aqueous phase using H_2PdCl_4 as precursors, NaH_2PO_2 as P sources and reduce agents. In a typical synthesis of $Pd_{86}P_{14}/NC$, 1.28 mL of H_2PdCl_4 (10 mM) were injected in 20 mL of H_2O with additional 6.0 mL of NC (8.0 mg mL⁻¹), and further stirred at room temperature for 30 min. Then, the solvent was removed under a high pressure. After that, 10 mL of NaH_2PO_2 (0.34 M) was injected into the above powder and reacted for 1 h. The products were finally collected via the centrifugation by water/ethanol for 3 times and dried at 35 °C in vacuum oven. PdP/NC with different diameters were synthesized by changing the H_2PdCl_4 concentrations, while PdP with different contents of P were obtained by changing the feeding ratios of NaH_2PO_2/H_2PdCl_4 . By contrast, Pd/NC was synthesized following the same procedures with PdP/NC, except replacing the NaH_2PO_2 by $NaBH_4$ (26 mg $NaBH_4$ dissolved in 10 mL of water) as the reductant.

Test of catalytic performance

In a typical test, 10 mg of catalysts were dispersed totally with 2.0 mL of water contained 1.0 M of formic acid and 3.0 M sodium formic in a 5.0 mL of single flask at 30 °C. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas (the temperature was kept constant at 30 °C during the measurements). The reaction started when 1.0 mL of mix solution of formic acid and sodium formic (FA/SF=1/3, [FA] = 1 M) was injected into the solution. The volume of the generated gas was monitored by recording the displacement of water in the gas burette. The procedures of kinetics under different concentrations of FA, SF, amounts of catalysts, and reaction temperatures were measured by the same procedures. The gases generated from the decomposition of FA were

analyzed by GC-8A TCD analyzers (Shimadzu), which was collected after purging the reactor with N_2 for three times.

TOF calculate method

TOF values were calculated by the method reported:²

$$TOF = \frac{P_{atm}V_{gas}/RT}{2n_{Pd}t}$$
 (equation S1)

Where P_{atm} is the atmospheric pressure (101325 Pa), V_{gas} is the final generated volume of (H₂ + CO₂) gas, *R* is the universal gas constant (8.3145 m³ Pa mol⁻¹ K⁻¹), *T* is the room temperature (298 K), n_{Pd} is the total mole number of Pd atoms in catalyst, and *t* is the completion time of the reaction in hour.

CO stripping and TPR measurement

The CO stripping voltammograms were obtained by the following procedures: the samples were saturated with carbon monoxide by bubbling the gas during 20 min at 0.15 V (vs SCE). The excess of CO was then eliminated from the electrochemical cell by purging the solution with pure N₂ during 30 min. Afterward, cyclic voltammograms were recorded at 0.05 V s⁻¹ in the potential range of -0.9-0.2 V (vs SCE). The first cycle provided the total charge of CO oxidation, while the others were taken to check the recovery of the original voltammetric profile. For TPR measurement, 100 mg of sample was packed into the reactor. After the pretreatment at 200 °C for 60 min, it was cooled to 50 °C. Then, the catalyst bed was heated from 50 to 800 °C with a heating rate of 10 °C min⁻¹. The signals were monitored by a thermal conductivity detector (TCD, Micromeritics AutoChem II 2920).

Characterizations

Transmission electron microscope (TEM) observations were performed with a JEOL JEM-2100 microscope operated at 200 kV. High-angle annular dark-field scanning STEM was taken on JEOL JEM-2100F microscope that are equipped with STEM and EDS detectors for elemental mapping analysis. TEM and STEM samples were prepared by casting a suspension of the samples on a carbon coated copper grid (250 mesh). X-ray diffraction (XRD) patterns were recorded on powder samples using a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite-monochromatized Cu Kα radiation. X-ray photoelectron spectra (XPS) were performed on a scanning X-ray microprobe (Thermo ESCALAB 250Xi) that uses Al Kα radiation. Binding energy of the C 1s peak (284.8 eV) was employed as a standard to calibrate binding energies of other elements.

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Figure S1. Supporting TEM images of PdP/NC with different magnifications. The results definitely exhibited the uniformity and purity of PdP nanoclusters supported on carbon support.



Figure S2. Nitrogen adsorption-desorption isotherms of PdP/NC.



Figure S3. TEM and STEM images of PdP/NC synthesized with different initial feed ratios of NaH₂PO₂/H₂PdCl₄ (in a fixed H₂PdCl₄ amount): (a,b) $0.6*10^3$; (c,d) $1.2*10^3$; (e,f) $7.05*10^3$; and (g,h) $11.75*10^3$, respectively.



Figure S4. TEM and STEM images of Pd/NC obtained by $NaBH_4$ as a reductant.



Figure S5. TEM images of PdP/NC with different diameters of (a), (b) PdP-0.85/NC; (c), (d) PdP-1.30/NC; (e) (f) PdP-1.93/NC; (g), (h) PdP-2.03/NC, respectively. The diameters of PdP/NC were increased with the feeding concentration of H_2PdCl_4 precursors in the synthesis.



Figure S6. (a), (b) TEM images of the PdP NPs without NC; (c) Volume of the generated gas $(CO_2 + H_2)$ versus time for the dehydrogenation of FA/SF, and (d) the corresponding TOF values (h⁻¹) of PdP/NC, commercial Pd/C and PdP NPs.



Figure S7. Gas chromatograms of reference gases (H_2 , CO, air) and the gas released from FA over the as prepared PdP/NC, Pd/NC, Commercial Pd/C catalysts at 303 K, there was no CO signal observed from FA over the three nanocatalysts.



Figure S8. Catalytic kinetics study of Pd/NC. (a) The corresponding Time-V(gas) plots of Pd/NC with different Pd concentration and (b) the relationship between In[Pd] vs InK, (c) the corresponding Time-V (gas) plots of Pd/NC with different temperature and the summarized TOF values (inserted in (c)), (d) the Arrhenius plot of In(TOF) versus 1/T of the catalyst of Pd/NC.



Figure S9. Catalytic kinetics study of commercial Pd/C. (a) The corresponding Time-V(gas) plots of commercial Pd/C with different Pd concentration and (b) the relationship between In[Pd] vs InK, (c) the corresponding Time-V (gas) plots of commercial Pd/C with different temperature.



Figure S10. Catalytic stability. (a) Time vs V (gas) plots of PdP/NC during reaction times (four times), and (b) corresponding summary of TOF values (h⁻¹) and P content in PdP (at.%).



Figure S11. TEM images of PdP/NC after (a), (b) first; (c), (d) twice; (e) (f) three times; (g) (h) 4 times durability tests for the dehydrogenation of FA, respectively.



Figure S12. Time vs V (gas) plots of (a) Pd/NC, (c) commercial Pd/C during reaction times (3 times); and corresponding TOF values (h⁻¹) summary of (b) Pd/NC, (d) commercial Pd/C.



Figure S13. TEM images of Pd/NC after (a), (b) first; (c), (d) twice; (e) (f) three times durability tests, respectively.



Figure S14. (a), (b) TEM images of commercial Pd/C, and the TEM images of commercial Pd/C after (c), (d) twice; (e) (f) three times; (g) (h) 4 times durability tests, respectively.



Figure S15. Size summaries of the diameters of PdP/NC, Pd/NC and commercial Pd/C after durability

tests.

Number	Catalyst	Additive	Temp. (°C)	TOF(h ⁻¹)	Ref.
1	PdP/NC	HCOONa	30	3253.0	This work
2	Pd/CN _{0.25}	None	25	752	3
3	PdAg-CeO2/MC	HCOONa	30	322	4
4	Pd/MSC-30	HCOONa	30	1059	5
5	Pd/PDA-rGO	HCOONa	50	3810	6
6	Pd-B/C	HCOONa	30	1184	7
7	AuPd- MnO _x /ZIF-8- rGO	HCOONa	25	382	8
8	$Ag_{0.1}Pd_{0.9}/rGO$	HCOONa	50	2739	9
9	0.8Pd0.2Ni(OH) 2@S-1	HCOONa	25	600	10
10	Pd/C	HCOONa	30	1733	11

Table S1. Summarizations of the activity of the dehydrogenation of FA by different kinds of catalysts.

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