Electronic Supplementary Information (ESI) for

Pd nanoparticles anchored on amino-functionalized hierarchically porous carbon for efficient dehydrogenation of formic acid at ambient condition

Zhenzhen Wang, Chunpeng Wang, Shanjun Mao, Yutong Gong, Yuzhuo Chen and Yong Wang*

Advanced Materials and Catalysis Group, Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou 310028, P. R. China

* Corresponding authors: Tel: (+86)0571-88273551; Fax: (+86)0571-88273551. Email addresses: chemwy@zju.edu.cn

Experimental section

Chemicals and Materials

α-Cellulose (50 µm) (AR), (3-Aminopropyl)trimethoxysilane (APTMS, 97%) PdCl₂ (Pd, 59-60%) and formic acid (FA, \geq 98%) were purchased from Aladdin Chemistry Co., Ltd. (NH4)₂C₂O₄·H₂O (AR), NaHCO₃ (AR) and NaBH₄ (AR, 96%) were purchased from Sinopharm Chemical Reagent Co., Ltd. 10 mg/mL PdCl₂ aqueous solution was prepared by dissolving PdCl₂ in 0.6 M HCl solution.

Catalyst preparation

Synthesis of hierarchical porous carbon materials (NHPC). NHPC were synthesized according to our reported work.⁷ In a typical synthesis process of NHPC, α -cellulose, NaHCO₃ and (NH₄)₂C₂O₄ (mass ratio 1:3:3) were physically mixed thoroughly, then the mixture was calcined at 800 °C for 1 h under N₂ atmosphere. After it was cooled to room temperature, the black power was dissolved in copious water and magnetically stirred for 24 h at room temperature. Subsequently, the solution was filtered and washed with deionized water until the pH of the filtrate reached 7. Finally, the target NHPC was obtained after the black residue was dried at 70 °C.

Synthesis of Pd/NHPC-NH₂. In a typical procedure for the preparation of Pd/NHPC-NH₂, APTMS (0.4 mL) was ultrasonically mixed with 0.2 g of NHPC in 50 mL of aqueous solution for 1 h, and was then transferred to a magnetic stirring apparatus for 5 h. Afterwards, 2 mL PdCl₂ aqueous solution (10 mg/mL) were added into the above mixture with magnetic stirring. After stirring for 5 min, 2 mL of freshly prepared NaBH₄ aqueous solution (28 mg/mL) was added into the above mixed

solution with magnetic stirring for 2 min. Finally, the resulting $Pd/NHPC-NH_2$ was gathered by filtering, washed with copious water, and dried at 60 °C in a vacuum oven. For comparison, Pd/NHPC were prepared using the same procedure without the addition of APTMS.

Synthesis of Pd/NHPC_{H2}. Typically, 0.2 g of NHPC in 50 mL of aqueous solution was ultrasonic for 1 h and was further stirred on the magnetic stirrer for another 5 h. Subsequently, 2 mL PdCl₂ aqueous solution (10 mg/mL) were added into the above mixture with magnetic stirring. After stirring for 5 min, the resulting products were collected through filtration. After drying, Pd/NHPC_{H2} catalysts were obtained via reduction with 50 ml/min H₂ at 200 °C for 5 h.

Characterization

Transmission electron microscopy (TEM) was performed on a Hitachi HT-7700 microscope with an acceleration voltage of 100 kV. High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field scanning TEM (HAADF-STEM) were carried out on a FEI Tecnai G2 F20 S-TWIN instrument with an accelerating voltage of 200 kV. BET specific surface area and interstitial porous structure were measured using a Micromeritics, ASAP 2020 HD88 analyzer. The powder X-ray diffraction (XRD) patterns were obtained using an Ultima TV X-ray di \Box ractometer with Cu K α radiation (1.54 Å). X-ray photoelectron spectra (XPS) were recorded using a Thermo ESCALAB 250XI with an aluminum node (Al 1486.6 eV) X-ray source. The XPS spectra were corrected by adjusting the C 1s peak to a position of 284.6 eV. Inductively coupled plasma atomic emission spectroscopy (ICP-

AES) was conducted on a PerkinElmer emission spectrometer. For H₂-TPR, 150 mg samples were pretreated in an Ar flow at 120°C for 2 h. Then, the samples were reduced in a flow of 50% H₂/Ar (30 mL/min) and the temperature was increased from 28 to 200 °C at a heating rate of 2 °C/min. The composition of generated gas from FA was determined by a Schimadzu gas chromography with a TCD.

Catalytic tests

The dehydrogenation reaction of FA was carried out in a two-necked round bottom flask, connected to a reflux pipe and a gas burette. Typically, 0.044g catalyst and 2.0 mL of water were mixed for at least 15 min in a 25 mL two-necked round bottom flask in advance, which was placed in an oil bath at a preset temperature of 298 K. Next, one neck was connected to a gas burette for measuring the volume of the gas released from the reaction at certain time intervals. Then, 0.5 mL FA aqueous solution (5 M) was injected into the reaction flask by a syringe through the rubber stopper plugged in the other neck. The catalytic reaction was performed once the introduction of FA aqueous solution with magnetic stirring. The generated gas mixture was analyzed by GC.

Recycling stability of Pd/NHPC-NH2

For testing the durability of Pd/NHPC-NH₂, the catalyst was recollected from the reaction mixture by filtering after the completion of previous catalytic reaction cycle and washed with copious deionized water. Then, the dried catalysts were re-dispersed into the reaction system (1 M FA, 2.5 mL, $n_{Pd}/n_{FA} = 0.01$). Such test cycles of the catalyst for FA dehydrogenation were carried out for 5 runs at 298 K.



Fig. S1 High-resolution N 1s spectra of Pd/NHPC (a) and Pd/NHPC-NH₂ (b).

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
NHPC	681	0.549	15.9
NHPC-NH ₂	476	0.404	3.78

Table S1 Textural properties of HPC, NHPC and NHPC-NH $_2$.

Table S2 Comparison of the catalytic performance of $Pd/NHPC-NH_2$ presented in this work with the recently reported heterogeneous catalysts for H_2 release from FA in the absence of any additives at 298 K.

0.4.1.4	Т	TOF _{initial}	Ea ^{app}	Def	
Catalyst	(K)	(h ⁻¹) ^a	kJ mol ⁻¹	KeI.	
Pd/NHPC-NH ₂	298	1265	46.3	This work	
Pd/NHPC-NH ₂	298	3798 ^b	46.3	This work	
Pd/NMC-400°	298	913	36.86	S1	
Pd/SBA-15-NH ₂	298	127	-	S2	
Pd/CN _x ^b	298	639	48.8	S3	
Pd/NH ₂ -N-rGO	298	462.5	-	S4	
$Ni_{0.4}Pd_{0.6}/NH_2$ -N-rGO	298	954.3	-	S4	
Pd ₆₀ Au ₄₀ /ZrSBA-15-AP	298	1185	42.5	S5	
Ag@Pd/C	298	157	-	S6	
AgPd/C	298	274	22.0	S7	
AuPd/C	298	41	28.0	S8	
PdAu/N-SiO ₂	298	164	26.2	S9	
PdAu-MnO _x /N-SiO ₂	298	981	26.2	S9	
AgPd@MIL-100(Fe)	298	58	-	S10	
AgAuPd/rGO	298	95	-	S11	
Au@Pd/N-mrGO	298	111	-	S12	
AuPd-CeO ₂ /N-rGO	298	68	-	S13	
AuPd-MnO _x /ZIF-8-rGO	298	764	-	S14	
PdAg-MnO _x /N-SiO ₂	298	482	72.4	S15	
CoAuPd/C	298	54	-	S16	
NiAuPd/C	298	20	-	S17	
CrAuPd/N-SiO ₂	298	707	49.8	S18	
CoAuPd/DNA-rGO	298	130	-	S19	

 $^{\rm a}$ TOF_{initial} was calculated based on the total moles of noble metal in catalyst at 20%

conversion of FA according to the corresponding manuscript.

^b TOF was defined based on the mole of surface Pd.

^c TOF_{initial} was calculated based on the molar of Pd exposed on catalyst surface at 5.7% conversion of FA according to the corresponding manuscript.

Calculation method of initial TOF value:

The initial TOF value was calculated based on the molar amount of noble metal Pd and Au atoms according to the following equation:

$$TOF = \frac{P_0 V/2RT}{n_{metal} t}$$

wherein P₀ is the atmospheric pressure (101325 Pa), V is the volume of (H₂ + CO₂) released at 20% conversion of FA (m³), R is the universal gas constant (8.3145 m³ Pa mol⁻¹ K⁻¹), T is the room temperature (298 K), n_{metal} is the total mole number of noble metal atoms in catalyst, and *t* is the reaction time (h) when a 20% conversion of FA is reached.

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