Supporting Information

Biomass-derived ordered mesoporous carbon nano-ellipsoids encapsulated metal clusters inside: ideal nanoreactors for shape-selective catalysis

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Experimental

Materials

Xylose, $H_2PtCl_6 \cdot 6H_2O$, and $PdCl_2$ were purchased from Aladdin, Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) was purchased from Sigma-Aldrich, and concentrated sulfuric acid was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Characterization

Scanning electron microscopy (SEM) images were taken using a Hitachi SU-8010. Transmission electron microscope (TEM) measurements were carried out with a Hitachi HT-7700 microscope. Typically, several milligrams of sample were added into a tube with several milliliters of ethanol, then it was under ultrasound for 30 min. Finally, the ethanol solution contained sample was dropped on a carbon film coated grid and was dried under infrared lamp for about 1 h. Small-angle X-ray scattering (SAXS) was performed by XEUSS SAXS/WAXS SYSTEM. Nitrogen sorption isotherms were measured at 77 K using a Micromeritics ASAP 2020. Pore-size distribution was derived from the desorption branch using the Density Functional Theory (DFT) model and Barrett–Joyner–Halenda method. Power X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV operating at 40 kV and 20 mA with Cu K α radiation. The X-ray photoelectron spectra (XPS) was recorded on an Escalab 250Xi spectrometer, and the binding energy was calibrated by C1s peak (284.6 eV). The inductively coupled plasma-atomic emission spectrometry (ICP-AES) was carried out on a Perkin Elmer Optima OES 800.

Synthesis of ZJU-3 and C-ZJU-3. In a typical synthesis, 1.5 g of xylose and 3.0 g of F127 were dissolved in 54.5 mL of deionized water and 5.5 mL of concentrated H₂SO₄, stirring for 12 h. Then the mixture was measured with 10 mL and transferred to a 15 mL Teflon-lined stainless steel autoclave for hydrothermal treatment for 24 h at 150 °C. After cooling down to the room temperature, the products were collected by centrifuging and washed by water and ethanol for several times. The obtained ZJU-3 were dried in 70 °C overnight. C-ZJU-3 were produced by direct carbonization of asmade ZJU-3 at 350 °C for 1 h, then heating up to 550 °C followed by maintenance at 550 °C for 1 h in N₂ (99.99%) atmosphere with a heating rate of 1 °C min⁻¹.

Synthesis of Pt@ZJU-3, Pd@ZJU-3, Pt/Pd@ZJU-3, and Pt@C-ZJU-3. To encapsulate metals in ZJU-3, 160 μ L of H₂PtCl₆·6H₂O (10 mg/mL) or 100 μ L of PdCl₂·HCl (10 mg/mL) were added into a 15 mL Teflon-lined stainless steel autoclave before hydrothermal treatment. The other procedures were the same as those described for ZJU-3. To prepare Pt/Pd, 200 μ L of H₂PtCl₆·6H₂O (10 mg/mL) and 40 μ L of PdCl₂·HCl (10 mg/mL) were added together. The obtained Pt@ZJU-3 were dried in 70 °C overnight. Pt@C-ZJU-3 were produced by carbonization of as-made Pt@ZJU-3 at 550 °C in N₂ (99.99%) atmosphere and then at 350 °C in N₂ (99%) atmosphere for 1h.

Catalytic tests. In a typical process, 5 mL ethanol, and 10 mg catalysts (Pt@C-ZJU-3) were added into a 25 mL 3-necked round bottom flask and thoroughly mixed. Then 0.5 mmol substrate (4-nitrochlorobenzene/1-nitronaphthalene) was added. A balloon filled with H₂ was connected to the flask, and the flask was purged with H₂ for three times before reaction. Then, the reactor was placed in an oil bath and was maintained at 40 °C with a magnetic stirrer (800 rpm) for 1 h. After sampling and centrifugation, the product distribution of the solution was analyzed by gas chromatography-flame ionization detector (GC-FID). The reaction results were quantified by normalization method.

Catalyst reusing. In order to examine the stability of the catalysts, they were recycled in repeated runs. Parallel experiments were conducted during the recycling test. One 25 ml 3-necked round bottom flask, with a balloon filled with H₂, contained 0.5 mmol 4nitrochlorobenzene, 5 mL ethanol and 10 mg Pt@C-ZJU-3. Another, with a balloon filled with H₂, contained 20 mg Pt@C-ZJU-3 with 1.0 mmol substrates and 10 mL ethanol and was used as a catalyst supplier for the first flask. The catalytic hydrogenation was carried out at 40 °C for 1 h separately. After each run, the recovered catalyst was washed several times with ethanol and dried overnight at 60 °C. The mass loss of the catalyst in the first flask was supplied from the second flask before the next run. Subsequent reusability tests were carried out following the same procedures as stated above.



Figure S1. Characterization of ZJU-3. SEM (a) and TEM (b) images. Nitrogen adsorption-desorption isotherms (c) and pore size distribution curves (d).



Figure S2. TEM images of ordered mesoporous polymers prepared with different amounts (0.1, 1.6, 1.8 M) of sulfuric acid.

The products were prepared in different amounts of sulfuric acid. 0.1 M (59.5 mL of deionized water, 0.5 mL of concentrated H_2SO_4); 1.6 M (54.5 mL of deionized water, 5.5 mL of concentrated H_2SO_4); 1.8 M (54.0 mL of deionized water, 6.0 mL of concentrated H_2SO_4). In a typical synthesis, 1.5 g of xylose and 3.0 g of F127 were dissolved in different amounts (0.1, 1.6, 1.8 M) of sulfuric acid solution, stirring for 12 h. Then the mixture was measured with 10 mL and transferred to a 15 mL Teflon-lined stainless steel autoclave for hydrothermal treatment for 24 h at 150 °C.



Figure S3. SEM (a) and TEM (b) images of ordered mesoporous carbon prepared from HCl.



Figure S4. Thermogravimetric (TG) analysis of F127 (a). SEM (b) and TEM (c) images of C-ZJU-3 prepared by carbonization at 550 $^{\circ}$ C.



Figure S5. Nitrogen adsorption-desorption isotherms (a) and pore size distribution curves (b) of ordered mesoporous carbon prepared from HCl after carbonization at 550 $^{\circ}$ C.



Figure S6. XRD patterns of various metals encapsulated in ZJU-3.



Figure S7. (a) HRTEM image of a single Pt/Pd@ZJU-3 and (b) EDS spectra obtained along a line on the HRTEM image.



Figure S8.TEM images and Pt particle-size distribution of the control sample Pt/ZJU-3 before (a) and after (b) calcination at 550 °C.



Figure S9. TEM images of Pt nanoparticles reduced by xylose (a) and F127 (b) at 150 °C for 12 h. Photograph of the H₂PtCl₆ reaction solutions with and without xylose or F127 at 150 °C for 12 h (c). XRD patterns of Pt NPs reduced by xylose and F127 (d). XPS spectra of Pt 4f in the Pt NPs reduced by F127 (e). Photograph of the xylose reaction solutions with and without Pt precursor at 150 °C for 0.5 h (f). Upon the autoclaves cooled down, this photo was taken without centrifugation. We have attributed the turbidity in the sample with Pt precursor to the nucleation.

It should be noted that the products of Xylose-Pt and F127-Pt are turbidity solutions with few solids (Figure S9c). To obtain the data of XRD and XPS, 100 mg of activated carbon were added directly in the reaction solutions. The reaction mixture was stirred for 24 h. The products were separated by centrifugation. After drying under vacuum at 70 °C, the final products were tested.



Figure S10. TEM and SEM images of Pt@C-ZJU-3 before (a,c) and after (b,d) calcination at 550 °C.



Figure S11. Nitrogen adsorption-desorption isotherms (a), mesopores size distribution curve using the BJH model pore size distribution curves (b), and pore size distribution by DFT model (c) of Pt@C-ZJU-3. TEM image (d), nitrogen adsorption-desorption isotherms (e), and pore size distribution by DFT model (f) of commercial Pt/C.



Figure S12. Recyclability results of Pt@C-ZJU-3 catalyst (a). TEM image of Pt@C-ZJU-3 after 6 cycles (b). Reaction conditions: 4-nitrochlorobenzene (0.5 mmol), ethanol (5 mL), catalyst (10 mg), 40 °C, P_{H2} = 1atm, and 60 min.

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	Sample	Carbon content (%)	Hydrogen content (%)	Oxygen content (%) ^[a]
-	ZJU-3	64.7	4.7	30.6
	C-ZJU-3	83.7	2.8	13.5
-				

Table S1: Element analysis of ZJU-3 and C-ZJU-3

[a] O (%)=100% – C (%) – H (%)

Table S2: Activity of catalysts treated differently.

Processes	Temperatur	Temperature	Temperature	Activity in
Catalyst	e of HTC	of calcination ^a	of calcination ^b	reaction ^c
Pt@ ZJU-3	150	×	×	×
Pt@C-ZJU-3-(1)	150	550	×	×
Pt@C-ZJU-3-(2)	150	550	280	×
Pt@C-ZJU-3-(3)	150	550	300	×
Pt@C-ZJU-3-(4)	150	550	320	×
Pt@C-ZJU-3	150	550	350	√ (94%)

^a Calcination is under N_2 (99.99%).

^b Calcination is under N₂ (99%).

° Reaction conditions: 4-nitrochlorobenzene (0.5 mmol), ethanol (5 mL), catalyst (10 mg), 40 °C, P_{H2} = 1atm, and 60 min.

Table S3: Dispersion and metal surface area of Pt for Pt@C-ZJU-3.

Sample	Pt	CO	Metal	Metal	Theoretic	Metal
	loading	uptake	area	dispersion	al metal	exposure
	(wt %) ^b	(µmol/g _{ca}	$(m^2/g_{Pt})^d$	(%) ^e	dispersio	degree
		t.) ^c			n (%) ^f	(%) ^g
Control sample ^a	0.5	0.17	0.35	0.14	>25	< 0.56
Pt@C-ZJU-3	0.5	5.55	59.8	22	25	88

^aControl sample were produced by carbonization of as-made Pt@ZJU-3 at 550 °C in N_2 (99.99%) atmosphere.

^bCalculated by ICP-AES.

^cg_{cat.} is the weight of catalyst used in CO chemisorption.

CO uptake = $n_{CO} / m_{cat.}$

^dg_{Pt} is the actual weight of Pt in the catalyst.

Metal area = ($S_{metal} \times n_{CO} \times N_A$)/($m_{cat.} \times meatal loading$)

^eMetal dispersion D = ($n_{CO} \times M_{Pt}$ / ($m_{cat} \times$ meatal loading)

^fTheoretical metal dispersion $Dt = 5 \times M_{Pt} / (\rho \times N_A \times S_{metal} \times d)^{[1]}$

^gMetal exposure degree = D/Dt

In the pulse CO chemisorption experiments, it can be assumed CO:Pt stoichiometry of 1:1. n_{CO} is the mol amount of adsorbed CO, $m_{cat.}$ is the weight of catalyst used in the experiment, S_{metal} is the cross-sectional area of Pt (0.089 nm²), N_A is Avogadro's constant (6.022×10²³ mol⁻¹). M_{Pt} is the atomic weight of Pt (195.1). ρ is the density of Pt (21.37 g/cm³). d is the average Pt particles size (3.4 nm).

Table S4. Pt content of Pt@C-ZJU-3 by ICP-AES analysis.

Catalyst	Mass content	Concentration	Volume	Mass
Pt@C-ZJU-3	0.5%	7.819 mg/L	100 mL	152 mg
After 6 cycles	0.5%	4.686 mg/L	50 mL	43 mg

 $^{\left[1\right] }Spenadel L. and Boudart, M., J. Phys. Chem. 1960(64) , 204$