Supporting Information

Covalent Triazine Frameworks with Palladium Nanoclusters as Highly Efficient Heterogeneous Catalysts for Styrene Oxidation

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Experimental Section

Materials

Reagents and chemicals were obtained from Shanghai Aladdin Bio-Chem Technology Co., LTD. without further purification.

Typical procedures for oxidation of olefins to the corresponding aldehyde compounds

Add styrene, catalyst (5 mol%), styrene (1 mmol), H_2SO_4 (70 wt%, 0.2 mmol) and MeCN (5 mL) to 25 mL two-neck flask, respectively. Then, H_2O_2 (30 wt%, 6 mmol) was added dropwise from the separatory funnel, and the mixture was heated to 65 °C. After the reaction was completed, the organic solvent was extracted, concentrated under reduced pressure.

Preparation

Synthesis of DCP-CTF: The DCP-CTF was prepared according to previous literature.^{S1} 2,6-Pyridinedicarbonitrile (DCP, 129 mg, 1 mmol) and zinc chloride (ZnCl₂, 681.5 mg, 5 mmol) were put into Pyrex tube. The Pyrex tube was evacuated, sealed, and heated to 400 °C for 10 h and then heated 600 °C for 10 h. The heating rate is 5 °C min⁻¹. The Pyrex tube was opened when it was cooled to room temperature. The black powder was treated with deionized water and dilute hydrochloric acid (1 mol L⁻¹). Then, the filtered black powder was washed in turn with deionized water (3×10 mL), THF (3×10 mL), and acetone (3×10 mL). Finally, the product was dried in vacuum at 100 °C for 24 h.

Synthesis of DCP-CTF@Pd-MC: The palladium acetate powder (13 mg, 0.058 mmol) was dissolved in dichloromethane (15 mL) and the solution was stirred for 30

min, then the DCP-CTF (90 mg) was added in the solution. After that the mixture was stirred for 24 h at room temperature. The obtained solid was centrifuged and extracted with dichloromethane soxhlet for 24 h. Then, DCP-CTF@Pd was dried under vacuum at 80 °C overnight. The Pd content was 7.45% as determined by ICP.

Instrumental characterization

Power X-ray diffraction (PXRD) data were collected with a PANalytical X'Pert Pro Diffractometer (Cu K α , $\lambda = 0.1542$ nm), transmission electron microscope (TEM) images were obtained on a transmission electron microscope (JEOL, JEM-2100). The morphologies of the samples were recorded by a JEOL scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer. X-ray photoelectron spectroscopy (XPS) data were obtained with Thermo Scientific K-Alpha spectrometer. Nitrogen sorption measurements were conducted with a Quantachrome Autosorb apparatus at 77 K. The specific surface areas were calculated by the Brunauer–Emmett– Teller (BET) method. The samples were degassed at 150 °C for 12 h before measurements. The Pd contents of the CTF samples were determined by ICP analysis with an Agilent 720ES. All experiments were monitored using thin-layer chromatography (TLC, hexane:ethyl acetate=2:1). The yield was determined by Agilent 19091J-413 gas chromatography based on the internal standard method.

Entry	H ₂ SO ₄ (equiv)	MeCN (mL)	H ₂ O ₂ (mmol)	Temp (°C)	Time (h)	Yield ^b (%)
1	0.2	5	6	rt	24	Trace
2	0.2	5	6	45	12	40
3	0.2	5	6	55	8	72
4	0.2	5	6	65	8	95
5	0.2	5	6	75	8	87
6	0.4	5	6	65	8	89
7	-	5	6	65	8	Trace
8	0.2	5	3	65	8	32%
9	0.2	5	12	65	8	39%
10 ^c	0.2	5	6	65	8	<50%
11	0.2	5	O ₂	65	8	Trace
12 ^d	Acid	5	6	65	8	<55%

 Table S1. The optimized the reaction parameters. ^a

^a Reaction conditions: styrene (1 mmol), H₂O₂ (30 wt%), catalyst (5 mol%), CH₃CN (5 mL), acid

(70% wt).

^{*b*} Determined by GC with an external standard.

^c With EtOH, MeOH, DMF, DMSO, Aceton, THF, Toluene, 1,4-dioxane as the solvent (5 mL).

^{*d*} With HCl, HNO₃ as the acid (70 wt%, 0.2 equivalent).



Figure S1. P–XRD patterns of DCP–CTF@Pd–MC (orange) and DCP–CTF@Pd–MC–5th (blue); simulated AA stacking of DCP–CTF (black).



Figure S2. The XPS spectra of (a) DCP-CTF@Pd-MC-5th. The deconvoluted (b) C 1s and (c) N 1s of DCP-CTF@Pd-MC-5th.



Figure S3. Average pore size distribution of DCP-CTF@Pd-MC (orange) and DCP-CTF@Pd-MC-5th (blue).



(a)





















(h)







(j)



Figure S4. GC spectra of (a) Benzaldehyde, (b) 4-Chlorobenzaldehyde, (c) 3-Chlorobenzaldehyde,

(d) 2-Chlorobenzaldehyde, (e) 4-Bromobenzaldehyde, (f) 4-Fluorobenzaldehyde, (g) 4-Tolualdehyde, (h) 4-Anisaldehyde, (i) 4-tert-Butylbenzaldehyde, (j) 4-Nitrobenzaldehyde, (k) Hexanal



Figure. S5. SEM image of DCP–CTF@Pd–5th (a). Mapping images of C (b), N (c), Pd (d).



 $\label{eq:Figure.S6} \textbf{Figure.S6}. \ N_2 \ adsorption/desorption \ isotherms \ of \ DCP-CTF.$



Figure S7. The recovery of the DCP-CTF@Pd-MC catalyst at different cycle times.

References

(1) Hug, S.; Stegbauer, L.; Oh, H.; Hirscher, M.; Lotsch, B. V. Nitrogen-Rich Covalent Triazine Frameworks as High-Performance Platforms for Selective Carbon Capture and Storage. *Chem. Mater.* **2015**, *27*, 8001–8010.