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Electronic Supporting Information

A novel cerium-based metal-organic framework supported Pd catalyst for semihydrogenation of phenylacetylene

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Materials: All the reagents were commercially available from Sigma-Aldrich Chemical Co. Ltd. and used as such without further purification.

Experimental

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) patterns were recorded using a Philips X'pert X-ray diffractometer (40 kV and 30 mA) using Cu K α radiation ($\lambda = 1.5406$ Å).

Brunauer-Emmett-Teller (BET) measurement

Gas sorption experiments were conducted using the Micrometric Tristar II plus. In a typical gas sorption experiment, the sample was activated under dynamic vacuum at 60 °C for 12 h. The N_2 adsorption isotherm was measured at 77 K, and the BET surface area and pore size distribution (PSD) plots calculated by the software incorporated in the Micrometric Tristar II plus.^{1,2}

Elemental analysis

Elemental analyses for C, H and N content of complexes were carried out using a CE-440 Elemental Analyser manufactured by Exeter Analytical. Element analysis for Ce was carried out using ICP-OES measurements on a Perkin-Elmer Optima 2000.

Thermogravimetric analysis (TGA) Measurements

Thermogravimetric analyses were carried out under a flow of air (5 mL min⁻¹) at a heating rate of 5 °C min⁻¹ on a Perkin-Elmer Pyris1 Thermogravimetric analyser. TGA data for Ce-bptc is shown in Figure S10.

X-ray photoelectron spectroscopy (XPS) measurement

XPS spectra were measured using a Kratos Axis Ultra instrument equipped with a monochromatic Al K α X-ray source (hv = 1486.6 eV). A charge neutraliser was used to minimise charging and spectra were aligned onto the binding energy scale relative to the hydrocarbon C-C/C-H peak at 284.8 eV. Spectra were fitted using the CASA XPS software using Voigt-like peak shapes. Spin-orbit splitting ratios and splitting energies were constrained to obtain physically meaningful fits using the NIST XPS database³

Scanning electron microscopy (SEM) imaging

SEM imaging and energy dispersive X-ray spectroscopy (EDX) analyses were performed using the FEI/Thermofisher Quanta 650 field emission gun SEM at the University of Manchester. The SEM

was equipped with a Bruker X Flash 6 | 30 silicon drift detector with Bruker ESPRIT EDX software v2.2. For high-resolution imaging, beam deceleration was employed to achieve a landing energy of 1 kV. For EDX analysis, beam conditions were set to 15 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and EDX elemental maps were collected on a Thermo Fisher Titan STEM (G2 80-200) equipped with a Cs probe corrector (CEOS), high-angle annual dark-field (HAADF) detector and ChemiSTEM Super-X EDX detector, operating at 200 kV.

Synthesis of Ce-bptc

Typically, 5.0 mg of biphenyl-3,3',5,5'-tetracarboxylic acid was dissolved in 1.2 mL DMF. $(NH_4)_2Ce(NO_3)_6$ (0.4 mL 0.533 M) in water was added to the DMF solution, and the mixture heated at 60 °C for 15 mins. The resultant precipitate was washed with DMF and acetone three times and dried in air. Yield: 35% (calculation based on cerium salt in the reaction). Elemental analysis for $\{Ce_6O_4(OH)_4(C_{16}H_6O_8)_3\cdot(H_3O)_{1.6}\cdot3DMF\cdot10H_2O\}$ calculated (Found) %: Ce, 35.3 (36.4); C, 28.8 (28.4); H, 2.87 (2.61); N, 1.76 (1.80).

Synthesis of Ce-UiO-66, Zr-UiO-66, and Zr-bptc

Synthesis and activation of Ce-UiO-66, Zr-UiO-66, and Zr-bptc were carried out using the reported methods.⁴⁻⁶ The successful synthesis of these materials was confirmed by PXRD and BET measurements.

Synthesis of Pd@Ce-bptc, Pd@Zr-bptc, Pd@Ce-UiO-66, Pd@Zr-UiO-66, Pd@CeO₂ and Pd@ZrO₂

The synthesis of the materials was carried out using literature reports.⁷ Typically, 200 mg of activated material was suspended in 20 mL n-hexane, and the mixture sonicated for 20 mins until it became homogeneous. After being stirred for around 30 mins, 0.16 mL of aqueous Pd(NO₃)₂ solution (50mg/mL) was slowly added dropwise with vigorous stirring. The resultant mixture was continuously stirred for 3 h and allowed to settle. The solid was collected from the supernatant fluid and dried in air at room temperature. The dried powder was reduced under 5%H₂/Ar for 2 h at 150 °C. Other catalysts were prepared using the same method but with different MOF supports.

Procedure for catalysis

Typically, 5 mg of catalyst and a magnetic stir bar were placed in a Schlenk tube, and the gas replaced by H₂ three times. THF (2.5 mL), 1 mmol of phenylacetylene, and 1 mmol of mesitylene were injected

into the Schlenk tube, and the mixture stirred at 700 rpm under H_2 at 25 °C. The reaction products were analysed by GC and GC-MS. For recycling tests, the reaction conditions remained the same except for use of the recycled catalyst. The conversion and selectivity were determined by GC-FID using mesitylene as the internal standard.

Structure determination and refinements of synchrotron PXRD data.

Synchrotron PXRD measurements were conducted at Beamline I11 Diamond Light Source (Oxford, UK) [$\lambda = 0.826562(2)$ Å]. Desolvated Ce-bptc was prepared by heating the as-synthesised sample at 60 °C under vacuum for 1 day. To prepare the substrate-loaded samples, a drop of phenylacetylene was added into the desolvated MOF (0.05 mmol). After being soaked for 10 hours, the powder sample was loaded in a 0.7 mm borosilicate glass capillary to prevent preferred orientations. High-resolution synchrotron PXRD data were collected in the 2 θ range of 0-150° with a step size of 0.001° using multi-analyser crystal (MAC) detectors at 25.0 °C.

TOPAS 5 was used to perform Pawley and Rietveld refinement on the PXRD patterns. Background, cell parameters and peak profile with Stephen model were first refined using Pawley refinement and then transferred to Rietveld refinement. The scale factor and lattice parameters were allowed to refine for all the diffraction patterns. The refined structural parameters include the fractional coordinates (x, y, z), the isotropic displacement factors for all the atoms, and the site occupancy factors (SOF) for the framework and guest molecules. The final stage of Rietveld refinement involved soft restraints to the C–C bond lengths within the benzene rings, and rigid body refinement was applied to the guest molecules in the pore. The quality of the Rietveld refinements was confirmed by the low weighted profile factors and the good fit to the data with reasonable isotropic displacement factors within experimental error

EPR spectroscopy

Continuous-wave EPR measurements were carried out at X-band (9.85 GHz) using an EMX Micro spectrometer (Bruker). Modulation amplitude of 0.9 mT was used with a microwave power of ~ 2.0 mW based on spectral lines saturation test. Strong pitch (g = 2.0028) was used as a standard reference. Theoretical modelling of EPR spectra was performed using the Easyspin toolbox package (Version 6.0.0) in MATLAB software (version R2020a). All reagents were deoxygenated under Ar. For *in situ* EPR measurements, α -phenyl N-tertiary-butyl nitrone (PBN) was dissolved in THF (0.2 mol/L) and used as a spin trap. Phenylacetylene (0.05 mmol), Pd@Ce-bptc (10 mol%, 0.005 mmol) were mixed

in the THF solution (3 mL) in a deoxygenated vial under Ar, followed by 0.1 mL of the PBN stock solution. 0.5 mL of the resultant PBN mixed solution was then transferred into a capillary for freeze pumping to further degas the solution to fully remove all dissolved gases. (< 0.01 mbar). The capillary was connected to a H₂ gas bag and directly used for EPR measurements. *In situ* EPR spectra of the reaction mixtures were collected before and after connection to the H₂ gas bag, and the reference experiment was conducted without adding alkyne substrate.



Figure S1. PXRD patterns of (a) Ce-bptc soaked in different solvents for 24 hours, and (b) with different Pd loadings.



Figure S2 PXRD patterns of (a) Pd@Ce-UiO-66, (b) Pd@Zr-UiO-66, (c) Pd@Zr-bptc before and after Pd loading and after the reaction.



Figure S3 (a) N_2 isotherms at 77 K and pore size distribution of (b) Ce-bptc and (c) Pd@Ce-bptc.



Figure S4 (a) N₂ uptake at 77 K and pore size distribution of (b) Zr-bptc and (c) Pd@Zr-bptc.



Figure S5 (a) N₂ uptake at 77 K and pore size distribution of (b) Zr-UiO-66 and (c) Pd@ Zr-UiO-66.



Figure S6 (a) N_2 uptake at 77 K of Ce-UiO-66 and Pd@Ce-UiO-66. Pore size distribution of (b) Ce-UiO-66.

a Fresh Ce-bptc



b Pd@Ce-bptc



Figure S7 SEM images of (a) Ce-bptc and (b) Pd@Ce-bptc.

SEM image Pd@Ce-bptc







25nm





Figure S8 EDX mapping of Pd@Ce-bptc.

a Fresh Ce-UiO-66



Figure S9 SEM images of (a) Ce-UiO-66 and (b) Pd@Ce-UiO-66.



Figure S10 TGA results for (a) Ce-bptc and (b) Pd@Ce-bptc.

The first weight loss (12.3%) below 200 °C corresponds to the removal of adsorbed solvent molecules in the pores of the MOF. The second weight loss (44.0%) at 250-400 °C corresponds to the decomposition of the MOF: 47.9% weight loss from $Ce_6O_4(OH)_4$ (BPTC)₃(H₃O)_{1.6} to (CeO₂)₆.



Figure S11 XPS spectra of (a) Ce-bptc, Pd@Ce-bptc, (b) Pd@Ce-UiO-66, and Pd@CeO₂, and (c) Pd@Zr-bptc.



Figure S12 XPS Pd 3d spectra of (a) Pd@Zr-bptc, and (b) Pd@Ce-UiO-66. The spectrum in (a) contains overlapping peaks of Zr 3p (red lines).



Figure S13 GC analysis of the liquid mixture from semi-hydrogenation of phenylacetylene. Reaction conditions: 5 mg MOF, 1 mmol phenylacetylene, 1 mmol mesitylene, 2 mL THF, 25°C, 2.5h.



Figure S14 PXRD patterns of as-synthesised and used Pd@Ce-bptc catalysts.



Figure. S15 Recycling test of semi-hydrogenation of phenylacetylene using Pd@Zr-bptc. Reaction conditions: 5mg MOF, 1mmol phenylacetylene, 1mmol mesitylene, 2mL THF, 25°C, 2.5h.



Figure S16 GC-FID standard curve for (a) phenylacetylene, (b) styrene, and (c) ethylbenzene.



Figure S17 GC-FID standard curve for (a) 4-chlorophenylacetylene, (b) 4-chlorostyrene, and (c) 4-chloroethylbenzene.



Figure S18 GC-FID standard curve for (a) 4-bromophenylacetylene, (b) 4-bromostyrene, and (c) 4-bromoethylbenzene.



Figure S19 GC-FID standard curve for (a) 4-methylphenylacetylene, (b) 4-methylstyrene, and (c) 4-methylethylbenzene.



Figure S20 GC-FID standard curve for (a) 4-*tert*-butylphenylacetylene, (b) 4-*tert*-butylstyrene, and (c) 4-*tert*-butylethylbenzene.





Figure S21 Synchrotron PXRD pattern for Ce-bptc and phenylacetylene-loaded Ce-bptc. Experimental data shown in black, Rietveld refinement model in red, and difference pattern in blue.



Figure S22 *In situ* X-band EPR spectra using PBN as spin trap. Experimental and simulated spectra of (a) $Pd@Ce-bptc + H_2 + phenylacetylene + PBN and (b) PBN in THF solution.$

 Table S1 Crystallographic data for Ce-bptc and phenylacetylene@Ce-bptc.

Sample Name	Ce-bptc	Phenylacetylene@ Ce-bptc
CCDC number	2205374	2205379
Crystal system	Cubic	Cubic
Space Group	Im-3	Im-3
Formula	Ce ₆ O ₄ (OH) ₄ (bptc) ₃	Ce ₆ O ₄ (OH) ₄ (bptc) ₃ (C ₈ H ₆) _{0.75}
a (Å)	25.1845(7)	25.2406(7)
beta (°)	90	90
Cell Volume /Å ³	15973.5(14) Å ³	16080.6(14) Å ³
Cell density g/cm ³	1.739	1.734
Method	Rietveld	Rietveld
R _{wp} (%)	7.226	7.184
$R_{\rm exp}(\%)$	3.868	4.117
GOF	1.868	1.745

 Table S2 Parameters for spintrap experiments with Pd@Ce-bptc.

	Adducts	g factor	A ¹⁴ N / G	A ^α H1 / G	A ^α H2 / G	lw/mT	Weighting	
	PBN-H	2.0055	15.0	7.4	7.4	0.50	0.89	
Pd@Ce-bptc+H ₂ +PBN						0.20		
	PBN-	2.0060	13.7	2.3	/	0.0	0.11	
	OOH					0.18		
Pd@Ce-bptc+H ₂ +substrate+PBN	PBN-	2.0060	13.7	2.3	/	0.06	1.00	
	OOH					0.15		
PBN (0.4 M THF solution)	PBN-	2.0060	13.7	2.3	/	0.06	1.00	
	OOH					0.15		

 Table S3 Comparison of the catalytic activity of reported materials.

No.	Catalysts	Tem p (°C)	P(H ₂) (bar)	T (h)	Conv (%)	Sel. of alkene (%)	TOF (h ⁻¹)	Cycle tests	Ref
1	Pd@Ce-bptc	25	1	2.5	99	93	396	Conv.: 1st 99%-5th 97% Sel.: 1st 92%-5th 94%	This work
2	Pd@Zr-bptc	25	1	2.5	99	91	391	Conv.: 1st 99%-5th 88% Sel.: 1st 92%-5th 96%	This work
3	Pd@Ce-UiO-66	25	1	3	99	88	353		This work
4	Pd@Zr-UiO-66	25	1	6	99	71	122		This work
5	Pd-Pb(27%) alloy NCs	25	1	7.5	99	91			8
6	Lindlar catalyst	40	1	23.3	100	88	30		9
7	Fe ₃ O ₄ @ZIF-8/Pd	40	1	4.5	100	91	154	Conv.:1st 100%-5th 100% Sel.: 1st 93%-5th 93% at 1.67h	9
8	PdZn _{0.6} /Al ₂ O ₃	40	1	2.1	100	86	4318	Conv.: 1st 92%-5th 92% Sel.: 1st 91%-5th 89%	10
9	Pd NCs@NCM	25	1	5	99	95	380	After 24 h reaction: Sel.: 87%	11
10	Pd/ZnO@C	30	1	1	96	99	733	Conv.: 1st 96%-5th 96% Sel.: 1st 99%-5th 99%	12

11	Pd@MPSO/SiO ₂ -1	30	1	2	99	97	248	Conv.: 1st 99%-5th 99% Sel.: 1st 97%-5th 97%	13
12	Pd/pph3@FDU- 12	25	1	8	92	94	560		14
13	Pd@mpg-C ₃ N ₄	30	1	1.4	99	94	771	Conv.: 1st 95%, 70 min-9th 85%, 140 min Sel.: 1st 95%-9th 96%	15
14	Pd+PEI@HSS	30	1	4.5	99	91	44		16
16	Pd/IL/Cu(BTC) ₃	30	1	0.6	99	99	2287	Conv.: 1st 99%-5th 95% Sel.: 1st 99%-5th 99%	17
17	Pd/NHPC- DETA-50	35	1	0.33	99	95	2872		18
18	1.3Pd– 3.6Cu ₂ O/TiO ₂	30	1	1.5	100	98	353		19
19	Pd@Ag-in-UiO- 67	25	1	1.6	100	91	80		20

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