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Supplementary Information for

Direct visualisation of metal-defect cooperative catalysis in Ru-doped defective MOF-808

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Supplementary Methods

1. MOF synthesis

The pristine and defective MOF-808 were prepared by solvothermal synthesis, based on an established method.¹ For pristine MOF-808, zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 1.944 g, 6 mmol), trimesic acid (or benzene-1,3,5-tricarboxylic acid, H₃BTC, 0.424 g, 2 mmol), dimethylformamide (DMF, 96 mL), and formic acid (84 mL) were sealed in a 250 mL glass bottle and heated at 125 °C for 48 h. After cooling to room temperature, the white solid product was centrifuged. The sample was exchanged with DMF 3 times and with ethanol 3 times over 4 days. The final product was then dried at 150 °C under vacuum.

Defective MOF-808 was prepared by replacing 25% or 50% of H_3BTC with equimolar amounts of pyridine-3,5-dicarboxylic acid (H_2PyDC) or isophthalic acid (or benzene-1,3-dicarboxylic acid, 1,3- H_2BDC). The remaining synthesis steps were kept the same as for the pristine MOF-808. The samples were labelled MOF-808-25N and MOF-808-50N for the samples with 25% and 50% H_2PyDC , respectively, and MOF-808-50C for the sample with 50% 1,3- H_2BDC .

Solvent-assisted linker exchange (SALE) was performed by dissolving a certain amount of pyridine-4-carboxylic acid (isonicotinic acid, HPyC) in 20 ml of DMF, then dispersing 100 mg of MOF-808 into the solution by sonication for 30 min. The suspension was heated at 125 °C for 24 h. The product was collected by centrifugation, washed with DMF 3 times and with ethanol 3 times, and then dried at 150 °C under vacuum. Samples are denoted as MOF-808-nPyC (n = 1, 2, 4), for which 25, 50, and 100 mg of HPyC were used, respectively.

2. Metal doping

Approx. 5 wt% of Ru was doped to the MOFs by the following method. 54.5 mg RuCl₃ was dissolved in 60 mL of acetone, then 400 mg of MOF was added and dispersed by sonication. The dispersions were stirred at room temperature for 48 h. The products were washed with acetone, collected by centrifugation, and then dried at 60 °C under vacuum.

3. Material characterisation

1) Hydrogen temperature-programmed reduction (H₂-TPR)

H₂-TPR was performed on a Quantachrome ChemBET Pulsar TPR/TPD analyser equipped with a cold trap. The detector current was set to 150 mA, and the H₂ flow rate was 20 mL \cdot min⁻¹.

2) *Powder X-ray diffraction (PXRD)*

PXRD was performed by using a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Cu K α 1 radiation (λ = 1.54056 Å).

3) Thermogravimetric analysis (TGA)

TGA was performed on a TA Instruments TGA Q600 under air at a flow rate of 100 mL \cdot min⁻¹ with a temperature range of 30 °C to 700 °C.

4) ¹H nuclear magnetic resonance spectroscopy (¹H NMR)

MOF-808 samples were digested by adding 0.5 mL of 0.1 M NaOH in D_2O to 10 mg of MOF followed by sonication for 45 min. This procedure dissolves the organic components of the MOF, and the inorganic portion remains as an insoluble residue. The mixtures were diluted with 1 mL D_2O and centrifuged to collect the clear supernatant solution. ¹H NMR spectra were recorded on a Bruker Avance III HD nanobay NMR equipped with a 9.4 T magnet at 400.2 MHz.

5) N_2 physisorption

The N₂ adsorption isotherms measured at 77 K and up to 1 bar were recorded on a Micromeritics Tristar instrument using ultrahigh purity N₂ (99.999%). Before the analysis, the sample (0.05-0.1 g) was loaded into the sample cell and was desolvated by subjection to a vacuum of 10–5 Torr at 150 °C for 1 h.

The Brunauer-Emmett-Teller (BET) surface areas were calculated through the use of the BET equation:

$$\frac{1}{v[(p_0/p)-1]} = \frac{c-1}{v_m c} \times \frac{p}{p_0} + \frac{1}{v_m c}$$
(1)

where *v* is the adsorbed quantity of gas, v_m is the volume of adsorbed gas in a monolayer, p_0 is the saturation pressure of the adsorbate, *p* is the equilibrium pressure, and *c* is the BET constant. A plot of $1/v[(p_0/p) - 1]$ on the y-axis and p/p_0 on the x-axis gives a linear region in the range $0.05 < p/p_0 < 0.3$, which can be used to calculate the monolayer coverage and consequently the surface area.

The micropore area and volume were calculated using the t-plot method.² The statistical thickness (t) of adsorbed N₂ is defined using the Harkins-Jura equation:

$$t = \left(\frac{13.99}{0.034 - \log(p/p_0)}\right)^{0.5}$$
(2)

For N₂, the relationship between t, v, and surface area (S) is given as:

$$t = 15.47 \left(\frac{\nu}{S}\right) \tag{3}$$

A plot of t on the x-axis against v on the y-axis shows a graph with two distinct regions, corresponding to the filling of pores ($t < \sim 3.5$ Å) and coverage of external surface ($t > \sim 3.5$ Å). The gradient of the latter section is used to determine the external surface area using Equation 3, which can consequently be used with the BET surface area to calculate the internal micropore area and volume.

6) Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS analysis of the samples was performed using an Agilent 7800 ICP-MS. The samples were digested in an acid solution (typically a mixture of 8 mL HNO₃, 1 mL H₂O₂, and 1 mL HCl). The acid digestion process was performed in a microwave system adjusted to 210 °C for 45 min at 1800W power. The samples were then filtered and diluted with MilliQ water prior to carrying out the experiments.

7) Scanning transmission electron microscopy (STEM)

Annular dark-field STEM images were obtained using the electron microscopy facility in Oxford. Energy-dispersive X-ray spectroscopy (EDS) mapping was used to depict the locations of different elements in the sample.

8) X-ray absorption spectroscopy (XAS)

XAS experiments were carried out at the TLS01C beamline of the Taiwan Light Source. Fluorescence mode was used for Ru K-edge measurements and achieved by using a silicon drift detector. The EXAFS data were analysed using IFEFFIT with Horae packages (Athena and Artemis).³

9) X-ray photoelectron spectroscopy (XPS)

XPS was performed by using a Thermo Scientific EXCAL LAB 250 XI spectrometer. The pass energy used for survey and region scans was 50 and 20 eV respectively. The energy resolution

for Ag $3d_{5/2}$ is ≤ 0.5 eV. During data analysis, peak positions were referenced to the C1s peak at 284.8 eV.

10) X-ray total scattering (XTS) with pair distribution function analysis (XPDF)

XTS data were collected at the I15 beamline of the Diamond Light Source. The calibrated wavelength was 0.161669 Å (76.69 keV). 2D scattering images were integrated into 1D datasets by FIT2D⁴ and converted to PDF by PDFgetX2 (*Q*-range = $0.4-25 \text{ Å}^{-1}$)⁵. PDFs were normalised by appropriate scaling constants so that their peak intensities are the same at the Zr···Zr correlation (*r* = 3.5 Å). Differential PDFs were obtained by subtracting the PDF of pristine MOF-808-50N from that of MOF-808-50N-Ru. The structural model of Ru clusters was simulated within PDFgui,⁶ following a method for discrete nanomaterials.⁷ The starting model was from the Cambridge Crystallographic Data Centre.

11) High-resolution PXRD (HR-XRD)

HR-XRD experiments were conducted at the Materials Science powder diffraction station (X04SA) of Swiss Light Source and the powder diffraction beamline (BL02B2) of SPring-8. The calibrated wavelength was 0.708721 and 0.999888 Å (17.49 and 12.40 keV), respectively. Data collection was performed using a 1D MYTHEN II micro-strip detector.

Rietveld refinement⁸ was performed using TOPAS-Academic 6⁹. The background was described by a shifted Chebyschev function. A Thompson-Cox-Hastings pseudo-Voigt peak function was used to describe the shape of diffraction peaks. The scale factor was allowed to vary at all times. Refined structural parameters include the lattice parameters, the fractional coordinates (x, y, z), isotropic displacement factors (*Beq*), site occupancy factors (SOFs), the translation and rotation of the axes of the rigid bodies describing the guest molecules within the MOF structure. The rigid bodies were described by Z-matrix. The quality of the refinement was assured by a small weighted-profile *R*-factor (R_{wp}), a small goodness-of-fit (GOF) factor, and acceptable *B*eq within experimental errors. All the errors of the atom–atom distances were calculated using the following equation:

$$r_{\text{error}} = (x_{\text{error}})^2 + (y_{\text{error}})^2 + (z_{\text{error}})^2 \times r_{\text{measure}}$$
(4)

where r_{error} is the error of the measured atom-atom distance, x_{error} , y_{error} , z_{error} are the errors of the fractional coordinates (x, y, z) respectively, r_{measure} is the measured atom-atom distance.

12) Diffuse reflectance infrared Fourier transform spectroscopy (DRFIT)

For phenol-adsorbed samples, *in situ* DRFIT experiments were performed on a Nicolet iS50 FT-IR spectrometer with a high-temperature, high-pressure DRIFT reaction cell using a mercury cadmium telluride (MCT/A) detector. The resolution was 4 cm⁻¹. Each spectrum was scanned 64 times. The sample was first activated under N₂ flow at 150 °C until two consecutive spectra had no difference. The system was then cooled down to 25 °C. The background spectrum was taken under N₂. The N₂ flow was then directed to phenol for loading to the sample for 1 h. Physisorbed molecules were then purged by pure N₂. Spectra were taken at 25, 50, 75, 110, 150, 200, and 250 °C.

For CO₂-adsorbed samples, *in situ* DRFIT experiments were performed on a Bruker tensor 27 vertex 80v FTIR spectrometer with a Harrick reaction cell using a liquid N₂-cooled MCT detector. The resolution was 4 cm⁻¹. Each spectrum was scanned 32 times. The sample was activated at 150 °C for 2 h under a purging N₂ gas with a flow rate of 20 mL·min⁻¹ and then cooled back to room temperature for CO₂ gas exposure measurement. CO₂ was introduced with a flow rate of 20 mL·min⁻¹ and the IR spectra were recorded at different times. All IR spectra were recorded at room temperature.

4. Catalytic testing

1) Phenol hydrogenation

Prior to catalytic testing, samples were treated in 5% H₂ (N₂) with a flow rate of 30 mL·min⁻¹ at 250 °C for 4 h. To determine whether the conditions of the H₂ reduction procedure were suitable, MOF-808-Ru was analysed by H₂-TPR. The H₂-TPR signal showed a peak at 240 °C with a shoulder at 180 °C, which are likely to correspond to the reduction of ruthenium oxide and ruthenium oxychloride, respectively, to form Ru clusters or nanoparticles. These temperatures are higher than typical values found in the literature,¹⁰ indicating a strong Ru-support interaction, which is consistent with Ru binding onto the nodes. After the Ru reduction peaks, there was a negative peak at 270 °C corresponding to the desorption of H₂, followed by another peak at 350 °C indicating the reduction of the aromatic linkers.¹¹ Therefore, the temperature for the H₂ reduction procedure was chosen to be 250 °C, which is suitable for reducing the Ru species without causing hydrogenation of the linkers.

The aqueous-phase phenol hydrogenation tests were carried out in a 25 mL stainless steel cylinder reactor. 2 mL of deionised water, 50 mg of phenol, and 20 mg of catalyst were added to the reactor, which was purged 5 times with H_2 and then pressurised with H_2 to 2 MPa. The reactor was heated to 50 °C with a constant stir rate of 1000 rpm. After 30 min or 1 h, the reaction was quenched by cooling the reactor rapidly in an ice bath.

Diethyl ether was used to extract products for GC-MS analysis. 20 uL octane was added as the standard. The phenol conversion and product selectivity were measured by gas chromatography with mass spectrometry (GC-MS) on an Agilent Technologies 7820A GC System equipped with a DB-5 column and 5977A MSD. Turnover numbers (TON) are calculated as the moles of cyclohexanone product divided by the moles of metal in the catalyst.

2) CO_2 reduction

The gas-phase CO₂ reduction was carried out in a continuous flow reactor. In a typical experiment, 0.3 g of sample was loaded into the reactor with quartz wool packed at both ends. The sample was pretreated with H₂ (50 mL·min⁻¹) at 250 °C for 1.5 h. After the reactor cooled down to the reaction temperature (180 °C), the reactants, CO₂/H₂/N₂/CH₄ (23.1:68.85:7.95:0.1), were introduced. The flow rate was 20 mL·min⁻¹, leading to a gas hourly space velocity (GSHV) of 4000 mL·g¹·h¹. The reaction pressure was 3 MPa. The flow rate was controlled by Brooks mass flow controllers. The reaction temperature was controlled by a custom-made furnace. The reaction pressure was controlled by a Swagelok back pressure regulator. The products were analyzed online by an Agilent Technologies 8890 gas chromatograph equipped with a thermal conductivity detector and a flame ionization detector. The CO₂ conversion and CH₄ selectivity were calculated as follows:

Conversion (CO₂) =
$$\frac{n(CO_2 \text{ in feed}) - n(CO_2 \text{ remaining})}{n(CO_2 \text{ in feed})} \times 100\%$$
 (5)

Selectivity (CH₄) =
$$\frac{n(CH_4)}{n(\text{all products})} \times 100\%$$
 (6)

Note: Major products include CH₄, CH₃OH, and CO.

5. Computational details

The unit cell of MOF-808 was optimised using the PBE functional¹² with an energy cutoff of 400 eV. The periodic density functional theory (DFT) calculation was performed in the *Vienna ab initio Simulation Package* (VASP).^{13, 14} The valence–core interactions were described using the

projector-augmented wave (PAW) method.¹⁵ A $1 \times 1 \times 1$ *k*-point mesh was used for Brillouin zone integrations. The convergence criterion for electron minimization was set to 10^{-4} eV, and the Hermann–Feynman force criterion for each relaxed ion was set to 0.05 eV/Å. The optimised cell parameters (a = b = c = 24.38 Å; $\alpha = \beta = \gamma = 60^{\circ}$) are in good agreement with the experimental results.¹⁶

To reduce the computational cost, a cluster model of MOF-808 was constructed by extracting the $[Zr_6O_4(OH)_4(COO)_{12}]^{12^-}$ anion from the optimised periodic structure and capping the unsaturated sites with protons. The cluster model of MOF-808-50N was constructed by replacing one formate linker with a pair of H₂O and OH⁻. A Ru₇O₅H₁ cluster derived from experimental observation was introduced onto the MOF-808 and MOF-808-50N clusters to construct the MOF-808-Ru and MOF-808-50N-Ru clusters, respectively; these two models were used for further investigations. During geometry optimisations, the C atoms were fixed to retain the periodic constraints. The M06-L functional^{17, 18} and the def2-SVP basis set¹⁹ were used for the cluster calculations, which were carried out using the *Gaussian 16* program.²⁰

The adsorption energies of phenol were calculated as follows:

 $E_{\text{ads}} = E[\text{MOF-phenol}] - E[\text{MOF}] - E[\text{phenol}]$ (7)

where *E*[MOF–phenol], *E*[MOF], and *E*[phenol] are the DFT calculated energies of the phenol-adsorbed MOF system, the MOF, and a phenol molecule, respectively.

Supplementary Texts

Defective MOF-808 were also doped with Pd, Ni or Cu for their catalytic activity in phenol hydrogenation. For the Pd/Cu-doped catalysts, 1.8 mmol of $Pd(NO_3)_2 \cdot 2H_2O$ (479 mg) or Cu(NO- $_3)_2 \cdot 2.5H_2O$ (419 mg) were dissolved in 100 mL of acetone, then 500 mg of MOF was added and dispersed by sonication. The dispersions were stirred at room temperature for 24 h. The products were washed with acetone, collected by centrifugation, and then dried at 60 °C under vacuum. For the Ni-doped catalyst, 1.2 mmol of NiCl₂ \cdot 6H₂O (285.2 mg) was dissolved in 60 mL of DMF with 250 µL of triethylamine (NEt₃), then 250 mg of MOF was added and dispersed by sonication. The dispersions were stirred at 80 °C for 48 h. The products were washed with DMF and acetone, collected by centrifugation, and then dried at 60 °C under vacuum.

The metal-doped MOF-808-50N samples were investigated by PXRD. The majority retain good crystallinity, indicating that the framework structure was maintained. The one exception is that the diffraction pattern of Ni-doped MOF-808-50N shows a noticeable broadening of the peaks, meaning that the crystallinity of the framework structure had been lost. This is likely due to the alternative method for Ni doping carried out in accordance with the literature for doping first-row transition metals to MOFs; these methods typically have the inclusion of a base, such as NEt₃ which was used in this synthesis, as well as a higher temperature of 80 °C.²¹ The purpose of the base is to deprotonate the exposed $-OH_2$ groups on the nodes in order to facilitate the binding of the metal. However, it appears that MOF-808-50N was not stable in these conditions. The diffraction patterns do not show any obvious peaks associated with the metal salts used in each synthesis, demonstrating that there are not any large crystals of metal salt remaining trapped in the pores. There are also no peaks corresponding to the diffraction pattern of these transition metals in their elemental form, indicating that the metal species must be small and well dispersed such that they are undetectable by PXRD.



PXRD data of metal-doped MOF-808-50N samples.

The Pd/Cu/Ni-doped defective MOF-808 samples were tested for their catalytic performance in phenol hydrogenation. Prior to catalytic testing, samples were treated in 5% H₂ (N₂) with a flow rate of 30 mL·min⁻¹ at 250 °C for 4 h. 100 mg of catalyst and a higher temperature of 150 °C were used, and the reaction was stopped after 2 h. The first-row transition metals, Ni and Cu, displayed no activity. The Pd-doped MOF-808-50N was active with a TON of 0.88. In comparison, the Rudoped defective MOF-808 showed the highest reaction rates, with TONs ranging from 1.72 to 2.56 after only 30 min at 50 °C. Owing to the relatively high reaction rates over Ru-doped defective MOF-808, these catalysts were chosen as the focus of the investigation.

The recyclability of the catalysts was investigated by observing the PXRD patterns of the used catalysts, revealing that the Ru-doped catalysts had good stability compared to the Pd-doped ones. In the PXRD pattern of used Pd-doped MOF-808-50N, there is a peak observed at $2\theta = 40^{\circ}$, which corresponds to the (111) plane of Pd metal, and the other peaks are broader and less intense compared to the original MOF. This indicates that the facile reduction and sintering of Pd to form large particles can cause structural damage to the MOF support. Conversely, the PXRD pattern of used Ru-doped MOF-808-50N does not show any peaks corresponding to Ru metal, and the catalyst remains highly crystalline, demonstrating that it could have good recyclability.



PXRD data of used MOF-808-50N catalysts.

Note: the large background signal at $2\theta = 12.5^{\circ}$ for the metal-doped samples is due to the grease used on the sample slide.

Figure S1.

PXRD data of pristine and defective MOF-808 samples. The grey line is the simulated diffraction data based on the crystal structure of MOF-808.¹⁶



Figure S2.

Zr XPS spectra of MOF-808 and MOF-808-50N.

MOF-808







Figure S3.

TGA traces of MOF-808 samples.



Figure S4.

First derivative of TGA traces.



Temperature of the weight loss peaks and corresponding species.

Temp. (°C)	Species
90	Water
200 (small)	DMF
310	Formate
520	BTC
560	PyDC / 1,3-BDC

Figure S5.

¹H NMR spectrum of digested MOF-808.



The ¹H NMR spectra of the digested MOFs were used to determine the relative abundance of the organic species within the samples. Figs. S4–7 show the recorded ¹H NMR spectra for the pristine and defective MOF-808 samples, enlarged on the aromatic region to observe the relevant peaks for the linkers.

There are three prominent peaks observed in the spectrum of pristine MOF-808 (Fig. S4), which correspond to DMF (7.92 ppm), BTC (8.38 ppm), and formate (8.44 ppm). Small peaks can be seen on either side of these main peaks, which arise from the coupling of these protons to carbon-13.²² The spectra of the defective samples show additional peaks corresponding to the ditopic linkers, confirming that incorporation of these linkers has taken place. The spectra of MOF-808-25N (Fig. S6) and MOF-808-50N (Fig. S7) show additional peaks at 8.58 ppm and 9.01 ppm, corresponding to the protons labelled H1 and H2 on PyDC. The spectrum of MOF-808-50C (Fig. S8) has additional peaks at 8.58 ppm (triplet, larger coupling constant), 8.27 ppm (triplet, smaller coupling constant), 7.97 ppm (double doublet), and 7.51 (triplet, larger coupling constant), which are attributed respectively to H1, H1, H2, and H3 of 1,3-BDC.

The relative areas of the BTC and ditopic linker peaks are used to calculate the percentage incorporation of defects into MOF-808. The percentage content of each ditopic linker is given as an approximate value, since the peaks on the NMR spectra corresponding to the ditopic linkers are small, so their relative area is affected significantly by the background signal.

Figure S6.

¹H NMR spectrum of digested MOF-808-25N.



Figure S7.

¹H NMR spectrum of digested MOF-808-50N.



Figure S8.

¹H NMR spectrum of digested MOF-808-50C.



Figure S9.

PXRD data of Ru-doped MOF-808 samples.



Figure S10.

Annular dark-field STEM image (top) and EDS mapping images (bottom) of MOF-808-50N-Ru.



Note: only the images of this one sample are shown since the other MOF-808-Ru samples all display similar results.

Figure S11.

Ru XPS spectra of various MOF-808 samples.

MOF-808-Ru unreduced



MOF-808-Ru reduced



MOF-808-50N-Ru unreduced



MOF-808-50N-Ru reduced



Figure S12.

X-ray absorption near edge structure (XANES) spectra of MOF-808-50N-Ru (top) and MOF-808-Ru (bottom) before and after H_2 reduction, with Ru metal, RuCl₃, and RuO₂ as reference.





Figure S13.

Extended X-ray absorption fine structure (EXAFS) data of MOF-808-Ru before and after H_2 reduction.



Coordination environment of Ru in MOF-808-Ru, obtained from EXAFS.

	Path	Coordination number	Bond length (Å)	$\sigma^2 / 10^{-3}$	R	E_0 (eV)
Before	Ru–O	4.81 ± 0.69	2.09 ± 0.03	9.3 ± 1.7	1 8%	5
reduction Ru-	Ru–Cl	1.19 ± 0.39	2.45 ± 0.03	2.4 ± 2.2	1.0%	
After	Ru–O	5.19 ± 0.81	2.06 ± 0.02	14.6 ± 2.8	1 0%	2
reduction	Ru–Ru	3.99 ± 0.87	2.69 ± 0.01	10.1 ± 1.9	1.9%	Ζ

Figure S14.

XPDF data of MOF-808 and MOF-808-50N as well as MOF-808-50N-Ru before and after reduction.



Figure S15.

Comparison of MOF-808 and MOF-808-50N XPDF data.



Figure S16.

¹H NMR spectrum of digested MOF-808-50N-Ru.



Figure S17.

PXRD data of as-synthesised and used MOF-808-50N-Ru (after stability test in Table S5).



Note: the large background signal at $2\theta = 12.5^{\circ}$ is due to the grease used on the sample slide. The similarity between as-synthesised and used MOF-808-50N-Ru indicates that the catalyst is stable for our discussion. As we cannot find peaks of Ru metal, Ru clusters in the spent catalyst are expected to remain in sub-nanometer size.

Figure S18.

¹H NMR spectrum of digested MOF-808-1PyC-Ru.



Figure S19.

¹H NMR spectrum of digested MOF-808-2PyC-Ru.



Figure S20.

¹H NMR spectrum of digested MOF-808-4PyC-Ru.



Table S1.

Acids	pK _{a1}	pK _{a2}
H ₃ BTC	3.12 ²³	3.89 ²³
H ₂ PyDC	2.72 ²⁴	4.62 ²⁴
1,3-H ₂ BDC	3.46 ²³	4.46 ²³
Formic acid	3.75 ²⁵	-

 pK_a values of acids involved in the synthesis of MOF-808 samples.

Table S2.

	Path	Coordination number	Bond length (Å)	$\sigma^2 / 10^{-3}$	R	E_0 (eV)
Before	Ru–O	5.35 ± 1.00	2.06 ± 0.02	10.5 ± 2.1	1.0%	7
reduction	Ru–Cl	1.45 ± 0.39	2.49 ± 0.01	4.9 ± 2.2	1.0%	/
After	Ru–O	4.49 ± 0.61	2.02 ± 0.01	11.0 ± 2.2	0.8%	3
reduction	Ru–Ru	4.05 ± 0.65	2.68 ± 0.01	9.6 ± 1.3	0.0%	-3

Coordination environment of Ru in MOF-808-50N-Ru, obtained from EXAFS.

Table S3.

Crystallographic information of MOF-808-50N-Ru. (CCDC Number 2339668)

Space group: Fd-3mZa = b = c = 35.25 Å $\alpha = \beta = \gamma = 90 ^{\circ}$

	Element	Symmetry multiplicity	x	у	Z	Occupancy	Beq
Zr1	Zr	96	0.79658	0.22726	0.45342	1	1.00408
C1	С	96	0.78129	0.28129	0.38143	1	1.871277
C2	С	96	0.79564	0.29564	0.34434	1	1.871277
C3	С	96	0.77938	0.32807	0.32807	1	1.989712
01	0	192	0.79866	0.2534	0.39586	1	2.068669
O2	0	32	0.77813	0.27813	0.47187	0.5	1.594928
O3	0	96	0.76548	0.18441	0.48452	0.5	1.776529
O4	0	192	0.7808	0.1791	0.413	0.5	3.00036
06	0	192	0.7949	0.1819	0.409	0.5	5.211151
07	0	96	0.75995	0.19794	0.49005	0.5	1.697572
Ru1	Ru	192	0.744182	0.161403	0.387394	0.01	3.58464
Ru2	Ru	192	0.8107	0.166565	0.348022	0.01	3.58464
Ru3	Ru	192	0.754904	0.118598	0.323713	0.01	3.58464
Ru4	Ru	192	0.746593	0.194647	0.318919	0.01	3.58464
Ru5	Ru	192	0.821423	0.123732	0.284312	0.01	3.58464
Ru6	Ru	192	0.812771	0.198874	0.27949	0.01	3.58464
Ru7	Ru	192	0.756918	0.150623	0.255039	0.01	3.58464
Or2	0	192	0.843463	0.120329	0.331542	0.01	5
Or3	0	192	0.765797	0.102373	0.269392	0.01	5
Or4	0	192	0.710001	0.15936	0.347569	0.01	5
Or6	0	192	0.7677502	0.2420081	0.2730984	0.01	5
Or7	0	192	0.783894	0.184606	0.213057	0.01	5

Table S4.

Catalytic performance of various MOF-based catalysts in phenol hydrogenation.

Catalyst	Metal	Rea	ction t	ime (h);	Phenol	Cyclo-	Yield	Ref
	(wt%)	Rea	Reaction temp. (°C);			conversion	hexanone	(%) ^a	
		H ₂ I	oressu	re (MP	'a);	(%)	selectivity		
		Met	al/phe	nol (m	ol/mol %)		(%)		
MOF-808-	Ru (6.5)	0.5	50	2	2.42	58.5	5.5	3.22	This
Ru		1				93.5	0.8	0.75	work
MOF-808-	Ru (6.8)	0.5	50	2	2.53	66.7	6.5	4.34	This
25N-Ru		1				99.4	1.1	1.09	work
MOF-808-	Ru (6.0)	0.5	50	2	2.23	29.4	18.1	5.32	This
50N-Ru		1				65.9	7.4	4.88	work
MOF-808-	Ru (5.9)	0.5	50	2	2.19	28.2	22.0	6.20	This
50C-Ru		1				59.8	11.5	6.88	work
Pd/MOF-	Pd (0.5)	2	260	2	0.09	84.3	11.0	9.30	26
140-AA									
Pd/MOF-	Pd (2.0)	2	260	2	0.35	98.3	14.5	14.30	26
140-AA									
Pd/MOF-	Pd (3.8)	2	260	2	0.67	96.6	12.1	11.70	26
140-AA									
Pd@HPUiO-	Pd (3.0)	1	80	0.1	6.73	14.8	94.2	13.94	27
$\mathrm{NH_2^b}$									
Pd@UiO-	Pd (2.9)	1	80	0.1	6.48	28.5	95.1	27.10	27
$\mathrm{NH_2^b}$									
Pd@UiO ^b	Pd (5.6)	1	80	0.1	12.62	51.4	92.9	47.75	27
Pd-UiO-66	Pd (2.0)	2	120	2	1.77	100	10	10.00	28
Pd-UiO-66-	Pd (2.0)	11	25	0.1	1.77	20	90	18.00	28
NH_2									
Ru/MIL-101	Ru (5.0)	4	50	0.7	5	99	25	24.75	29
Pd/MIL-101	Pd (4.9)	4	50	0.5	1.84	99.6	80.3	79.97	30
Pd(1.5)/MIL-	Pd (0.8)	5	70	0.34	4.74	10	10	1.00	31
125-NH-									
CH ₂ OH									
Pd/MIL-53	Pd (4.3)	2	50	0.5	1.62	45.7	98.6	45.06	32

^a Yield = conversion × selectivity; ^b cyclohexane as the reaction solution.

Table S5.

Cycle	Phenol conversion (%)	Cyclohexanone selectivity (%)	Cyclohexanone turnover number
1	29.4	18.1	2.38
2	28.6	18.8	2.40
3	25.3	21.1	2.39
4	21.8	24.3	2.37

The reusability of MOF-808-50N-Ru.

Note: Reaction time = 0.5 h

Table S6.

Catalyst	Ru content (wt%)	Phenol conversion (%)	Cyclohexanone selectivity (%)	Cyclohexanone turnover number
MOF-808-50N-Ru-1	1.7	11.8	52.9	9.85
MOF-808-50N-Ru-5	6.0	29.4	18.1	2.38
MOF-808-50N-Ru-10	9.9	94.2	1.2	0.31

Catalytic performance of MOF-808-50N-Ru with varied Ru content.

Note: Reaction time = 0.5 h

Table S7.

Sample	BET Surface Area $(m^2 \cdot g^{-1})$	t-Plot Micropore Area $(m^2 \cdot g^{-1})$	t-Plot Micropore Volume (cm ³ ·g ⁻¹)
MOF-808-Ru	596.5	199.8	0.12
MOF-808-50N-Ru	684.0	249.3	0.15

Porosity data of MOF-808-Ru samples.

Table S8.

Porosity data of MOF-808 samples.

Sample	BET Surface Area $(m^2 \cdot g^{-1})$	t-Plot Micropore Area $(m^2 \cdot g^{-1})$	t-Plot Micropore Volume (cm ³ ·g ⁻¹)
MOF-808	1336.6	1131.4	0.56
MOF-808-50N	1482.8	1271.8	0.62

Table S9.

Crystallographic information of phenol-adsorbed MOF-808-50N-Ru. (CCDC Number 2339670)

Space group: <i>Fd</i> -3 <i>m</i> Z	
a = b = c = 35.15 Å	
$\alpha=\beta=\gamma=90~^{\rm o}$	

	Element	Symmetry multiplicity	x	у	Z.	Occupancy	Beq
Zr1	Zr	96	0.79658	0.22726	0.45342	1	1.00408
C1	С	96	0.78129	0.28129	0.38143	1	1.871277
C2	С	96	0.79564	0.29564	0.34434	1	1.871277
C3	С	96	0.77938	0.32807	0.32807	1	1.989712
01	0	192	0.79866	0.2534	0.39586	1	2.068669
O2	0	32	0.77813	0.27813	0.47187	0.5	1.594928
03	0	96	0.76548	0.18441	0.48452	0.5	1.776529
O4	0	192	0.7808	0.1791	0.413	0.5	3.00036
O6	0	192	0.7949	0.1819	0.409	0.5	5.211151
07	0	96	0.75995	0.19794	0.49005	0.5	1.697572
Ru1	Ru	192	0.744182	0.161403	0.387394	0.01	3.58464
Ru2	Ru	192	0.8107	0.166565	0.348022	0.01	3.58464
Ru3	Ru	192	0.754904	0.118598	0.323713	0.01	3.58464
Ru4	Ru	192	0.746593	0.194647	0.318919	0.01	3.58464
Ru5	Ru	192	0.821423	0.123732	0.284312	0.01	3.58464
Ru6	Ru	192	0.812771	0.198874	0.27949	0.01	3.58464
Ru7	Ru	192	0.756918	0.150623	0.255039	0.01	3.58464
Or2	0	192	0.843463	0.120329	0.331542	0.01	5
Or3	0	192	0.765797	0.102373	0.269392	0.01	5
Or4	0	192	0.710001	0.15936	0.347569	0.01	5
Or6	0	192	0.76775	0.24201	0.2731	0.01	5
Or7	0	192	0.783894	0.184606	0.213057	0.01	5
pOC1	С	192	0.5472906	0.764071	0.4455526	0.2894	8.58464
pOC2	С	192	0.5253411	0.7414845	0.4672925	0.2894	8.58464
pOC3	С	192	0.5266175	0.7445216	0.5054199	0.2894	8.58464
pOC4	С	192	0.5498432	0.7701451	0.5218073	0.2894	8.58464
pOC5	С	192	0.5717926	0.7927316	0.5000674	0.2894	8.58464
pOC6	С	192	0.5705163	0.7896945	0.46194	0.2894	8.58464
pOO7	0	192	0.546	0.761	0.407	0.2894	8.58464

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