Enhanced Activity of Heterogeneous Pd(II) Catalysts on Acid Functionalized Metal–Ogranic Frameworks

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1. Methods and Instrumentation

**Materials.** Reagents and solvents were purchased from Fisher Scientific Co., Ltd., and Sigma-Aldrich Chemical Co., Ltd, and used without further purification. All gasses for activation and quantification were Ultra High Purity Grade 5.

**1H NMR.** NMR spectra was collected using 400 MHz Agilent DD MR-400 system.

**Diffuse Reflectance Infrared Fourier transform spectroscopy (DRIFTS).** DRIFTS spectra were recorded under Ar atmosphere on a Nicolet 6700 instrument (Thermo Scientific) equipped with an MCT detector and a Harrick praying mantis accessory. Prior to the measurements, the samples were heated 120 °C for 30 minutes with Harrick Scientific ATC temperature controller in a DRIFTS cell with ZnSe window under Ar flow. Anhydrous KBr powder was used as the background.

**Sorption study.** N₂ sorption isotherms were collected on a Micromeretics Tristar II 3020 instrument at 77 K. Prior to the measurement, the sample was activated on a SmartVacPrep port by heating at 120 °C under vacuum overnight. Pore-size distributions were calculated from these isotherms using DFT methods, based on molecular Statistical approach.

**Thermogravimetric analysis (TGA).** TGA curves were collected using a TA Instruments Q500 under a N₂ flow at a 10 °C/min ramp rate from 25 to 600 °C.

**Potentiometric titration.** Potentiometric titrations were carried out with a Metrohm Titrando 905 equipped with 800 Dosino dosing units (20 mL and 10 mL). Calibration was performed with commercial pH buffers of pH = 2.00, 4.00, 7.00, and 9.00 (Metrohm). Approximately 50 mg of MOF samples were dispersed in 50 mL of 0.01 M NaNO₃ aqueous solution overnight before titration. Each titration solution was charged with a magnetic stir bar, and then pH value was
adjusted to 2.5 using 0.1 M HCl aqueous solution. 0.1 M NaOH aqueous solution was used for titration of the MOF sample with the injection volume of 0.025 mL and an injection rate of 0.02 mL/min until the pH changes to 10–10.5. Equivalent points were estimated from the maximum points of the first derivatives of the resulting titration curve of pH as a function of volume of 0.1 M NaOH solution added. $pK_a$ values were determined as the pH at one-half of the volume of titrant added to reach the equivalence point. Curve-fitting analyses were performed using peak-o-mat software with Lorentzian functions.

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP–OES). ICP–OES spectra were recorded using a iCAP 7600 ICP–OES analyzer (Thermo Scientific) equipped with Varian Vista-MDX model ICP-OES spectrometer (Varian, Walnut Creek, CA) with a CCD detector and Ar plasma. The instrument was calibrated with standard solutions (1, 5, 10, 20, 40 ppm of analytes) prior to sample measurements. Samples (ca. 1 mg) were digested in nitric acid (70%, 0.75 mL) and hydrogen peroxide (35% in H₂O, 0.25 mL) at 150 °C for 5 min in a microwave reactor.

Transmission Electron Microscopy (TEM). TEM images were collected with a Hitachi HD-2300 Dual EDS Cryo STEM at an accelerating voltage of 200 kV. Samples were suspended in CH₂Cl₂ and sonicated 30 min to break the large crystals, and then, they were deposited on TEM grid (Formvar/Carbon, 400 mesh, Ted Pella).

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were carried out with a Thermo Scientific ESCALAB 250 Xi (Al Kα radiation, 1486.6 eV) operated at 14.6 kV and 11.5 mA. An equipped electron flood gun was utilized prior to scans. Samples were ground and spread on conductive carbon adhesive tape attached to sample holders. The carbon 1s binding energy of graphite in the carbon tape (284.6 eV) was used to calibrate the binding energy. Curve-fitting
analysis was performed using XPS PEAK4.1 software with a combination of Gaussian and Lorentzian line shapes.

**Raman Spectroscopy.** Raman spectra were recorded using an Acton Vista Confocal Raman Spectroscopy (S&I GmbH) with Olympus 100× microscope objective using a 632.8 nm laser.

**Single-crystal X-ray Crystallography.** X-ray crystal structure analysis was carried out using a Bruker Kappa APEX II CCD detector equipped Mo Kα (λ = 0.71073 Å) IμS microfocus source with MX optics. The single crystal was mounted on MicroMesh (MiTeGen) with paraton oil. The structure was solved by direct methods (SHELXT 2014/5)¹ and refined by full-matrix least-squares refinement on $F^2$ (SHELXL-2017/1)² using the Yadokari-XG software package.³ The disordered non-coordinated solvents were removed using the PLATON SQUEEZE program.⁴ Refinement result is summarized in Supporting Information Table S1 and S4. Crystallographic data in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-1901984-1901987. The data can be obtained free of charge via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

**Gas Chromatography with Flame Ionization detection (GC-FID).** GC-FID analyses were carried out with an Agilent 7820A GC system equipped with an Agilent J&W GC HP-5 capillary column (GC-Alumina, 30 m × 320 μm × 0.25 μm). The reaction profiles were calculated by measuring the components of aliquots taken at given times via GC-FID. All samples were filtered and diluted with acetone prior to injection. Gas chromatography mass spectrometry (GC-MS) analyses were performed on a time-of-flight GC mass spectrometer from Agilent 6890 GC.
2. Supplementary Discussions

2-1 Syntheses and Characterization of Acid Ligated MOFs

2-1-1 MOF Synthesis

**Hf-MOF-808.** Hf-MOF-808 was prepared by slightly modified published procedures for Zr-MOF-808.\(^5\) Prior to use, the glass vials were rinsed with Sigmaticote\(^6\) silicogenizing reagent to suppress the nucleation of crystals on the glass surface. HfOCl\(_2\cdot8\)H\(_2\)O (105 mg, 0.26 mmol) and benzene-1,3,5-tricarboxylic acid (H\(_3\)BTC: 54 mg, 0.26 mmol) were dissolved in DMF/formic acid (1:1, 20 mL), placed in screw-capped glass vial and heated at 120 °C for 5 days. The white crystalline powder was washed with fresh DMF three times. As-synthesized Hf-MOF-808 was suspended in 20 mL of DMF and 0.5 mL of 12M HCl, and heated 120 °C overnight to remove formic acid attached to the node. The complete removal of formic acid was confirmed by \(^1\)H NMR (Figure S1). The white crystalline powder was washed three time by fresh DMF (Hf-MOF-808 ([H\(_6\)(\(\mu\)\(_3\)-O)\(_4\)\(\mu\)\(_3\)-OH)\(_4\)(OH)\(_6\)(H\(_2\)O)\(_6\)(C\(_9\)H\(_3\)O\(_6\))\(_2\)]\(_z\)): Yield 55 mg, ca. 70% based on Hf)
Supporting Figure S1. $^1$H NMR spectrum of digested MOF sample before (blue) and after HCl wash (orange). Hf-MOF-808 samples were digested using D$_2$SO$_4$, and DMSO-$d_6$ was used as the solvent. The peak (*) comes from the DMF. The peak at 8.2 ppm and 8.7 ppm were attributed as C-H of formic acid, and aromatic C-H of H$_3$BTC, respectively. The removal of formic acid, which used as the synthetic modulators, was confirmed.
2-1-2 Acid Functionalization

\textit{Hf-MOF-808-PO}_4. The synthetic condition of phosphoric acid functionalization was tested with various concentration (0.01 ~ 0.1 M) of phosphoric acid aqueous solution (Figure S2), which indicated the loss of crystallinity more than 0.025 M of phosphoric acid. The final synthetic condition was as follows. The HCl-washed Hf-MOF-808 was solvent exchanged with acetone, and then with water for two days. The white crystalline powder (\textit{ca}. 100 mg) was suspended in 20 mL of 0.005 M H$_3$PO$_4$ aqueous solution (\textit{ca}. 3 PO$_4$ per node) for 2 hours at 0 ºC, and then washed by water three times. IR measurements indicated successful phosphoric acid incorporation (Figure S4). ICP measurement showed 2.2 P atoms per one Hf$_6$-node.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{pxrd.png}
\caption{PXRD pattern before and after phosphoric acid functionalization of Hf-MOF-808 with various H$_3$PO$_4$ concentration (more than 6 PO$_4$ per node conditions). Hf-MOF-808 sample (after HCl-wash) was soaked in phosphoric acid solution with various concentrations for 1 day.}
\end{figure}

\textbf{Supporting Figure S2.} PXRD pattern before and after phosphoric acid functionalization of Hf-MOF-808 with various H$_3$PO$_4$ concentration (more than 6 PO$_4$ per node conditions). Hf-MOF-808 sample (after HCl-wash) was soaked in phosphoric acid solution with various concentrations for 1 day.
**Hf-MOF-808-SO₄.** Hf-MOF-808-SO₄ were prepared by slightly modified published procedure.⁶ HCl-washed Hf-MOF-808 were solvent exchanged with acetone for two days, and then solvent exchanged with water for two days. The white crystalline powder (ca. 50 mg) was suspended in 20 mL of 0.1 M H₂SO₄ aqueous solution for 1 day, and then washed by water three times. PXRD measurement indicated no degradation of crystallinity (Figure S3). IR spectra also indicated successful sulfuric acid-ligation (Figure S4). ICP measurement showed 2.4 P atoms per one Hf₆-node.

![Supporting Figure S3. PXRD patterns before and after sulfuric acid functionalization.](image-url)
Supporting Figure S4. FTIR spectra. The black, blue, red curves showed the spectra of Hf-MOF-808, Hf-MOF-808-PO₄, and Hf-MOF-808-SO₄. For Hf-MOF-808-PO₄ and Hf-MOF-808-SO₄, the decreases in intensity of the peak associated with terminal and bridging $-\text{OH}$ stretches on the node at 3680 cm⁻¹ relative to Hf-MOF-808 was confirmed, suggesting a chemisorption of phosphate and sulfate species on the nodes of Hf-MOF-808-PO₄ and Hf-MOF-808-SO₄, respectively. The intense peak at approximately 1050 and 1200 cm⁻¹ could be assigned to the P=O and S=O stretching modes of coordinated phosphoric and sulfuric acid in Hf-MOF808-PO₄ and Hf-MOF808-SO₄, respectively. The sharp peak at approximately 1400 and 1600 cm⁻¹ could be associated to the C=C and C=O stretching modes of the BTC ligand, respectively, and the peak at approximately 780 cm⁻¹ is assigned as the bending vibration mode of the C-H of the BTC ligand.
Supporting Figure S5. (a) N₂ adsorption (filled symbol) and desorption (open symbol) isotherms of Hf-MOF-808 (black circle) and Hf-MOF-808-PO₄ (red square), and Hf-MOF-808-SO₄ (blue triangle). (b) DFT-calculated pore size distributions of Hf-MOF-808 (black circle) and Hf-MOF-808-PO₄ (red square), and Hf-MOF-808-SO₄ (blue triangle). The Brunauer–Emmett–Teller (surface) areas only decrease from 1450 to 1020 m²/g for Hf-MOF-808-PO₄ and from 1450 to 1130 m²/g for Hf-MOF-808-SO₄, indicating that porosity is retained during acid functionalization. In addition, DFT-calculated average pore size distribution showed only small decreases in their pore sizes.
2-1-3 SCXRD Analyses of Acid Ligated MOFs

**Figure S6.** Crystal structures of acid functionalized Hf-MOF-808s at 100 K. (a), (b) The side and top views of the node structure of Hf-MOF-808-PO₄. (c) The expected chemical structure of ligated phosphate. (d),(e) The side and top views of the node of Hf-MOF-808-SO₄. (f) The expected chemical structure of ligated sulfate. Phosphorous and sulfur sites are disordered between two crystallographically equivalent positions. Here, one orientations of phosphate and sulfate sites are shown for clarity. Spheres are gray (carbon), red (oxygen), cyan (hafnium), yellow (sulfur), and orange (phosphorous).
Supplementary Table S1 | Crystallographic data of acid functionalized MOFs

<table>
<thead>
<tr>
<th></th>
<th>Hf-MOF-808-PO$_4$</th>
<th>Hf-MOF-808-SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{18}$H$</em>{6}$O$_{32}$Hf$_6$(PO$<em>2$)$</em>{2.4}$</td>
<td>C$<em>{18}$H$</em>{6}$O$_{32}$Hf$_6$(SO$<em>2$)$</em>{2.4}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1956.30</td>
<td>1958.91</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Fd–3m (no. 227)</td>
<td>Fd–3m (no. 227)</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>35.140(3)</td>
<td>35.380(3)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>43390(11)</td>
<td>44273(94)</td>
</tr>
<tr>
<td>$Z$</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Calcd Density (g/cm$^3$)</td>
<td>1.198</td>
<td>1.176</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>5.796</td>
<td>5.691</td>
</tr>
<tr>
<td>$F$(000)</td>
<td>14022</td>
<td>14061</td>
</tr>
<tr>
<td>Crystal size (mm$^3$)</td>
<td>0.025 $\times$ 0.025 $\times$ 0.025</td>
<td>0.03 $\times$ 0.03 $\times$ 0.03</td>
</tr>
<tr>
<td>Total reflection</td>
<td>9321</td>
<td>15949</td>
</tr>
<tr>
<td>Unique reflection</td>
<td>1613</td>
<td>2130</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.1430</td>
<td>0.0696</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.013</td>
<td>1.091</td>
</tr>
<tr>
<td>$R_1$ [$I&gt;2\sigma(I)$]</td>
<td>0.0493</td>
<td>0.0355</td>
</tr>
<tr>
<td>$wR_2$ (all reflection)</td>
<td>0.1385</td>
<td>0.1026</td>
</tr>
<tr>
<td>CCDC</td>
<td>1901984</td>
<td>1901987</td>
</tr>
</tbody>
</table>
2-1-4. Acidity Evaluations

The acidity of Hf-MOF-808 and acid-functionalized Hf-MOF-808 were evaluated by the Hammett indicator base method and the potentiometric acid–base titration method.

In the Hammett indicator base method, the acid strength of a solid is defined as the ability of its surface to convert adsorbed neutral base B into its conjugate acid BH⁺, and is expressed by the Hammett indicator function⁶⁻⁸:

\[ H_o = -\log(a_{H^+} f_B / f_{BH^+}) = pK_{BH^+} - \log(C_{BH^+} / C_B) \]

where \( a_{H^+} \) is the activity of proton, \( pK_{BH^+} \) is the \( pK_a \) of the conjugated acid of the indicator, \( C_{BH^+} \) and \( C_B \) are the concentrations of B and BH⁺, and \( f_B \) and \( f_{BH^+} \) are their corresponding activity coefficients, respectively. If \( H_o \) of the acid sites on a solid surface lower than \( pK_{BH^+} \), the color of the basic indicator B changes to the color of BH⁺. Thus, the acidity of a solid can be estimated by the immersion of the solid in a solution of a specific indicator with the known \( pK_a \) value of its conjugated acid. Here, we employed three kinds of the Hammett indicators to evaluate the acidity of the synthesized MOFs. The Hammett indicator solutions (0.5 wt%) in benzene were prepared in an inert atmosphere. The activated MOFs (ca. 10 mg) were added to the solutions (2 mL), and the color change of the solid was recorded after a few hours. The results are summarized in Table S2.
Table S2. The Hammett indicator base test results. 

The test results are denoted as color change observed (+) and not observed (–)

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Colors of Acid form / Base form</th>
<th>$pK_a$</th>
<th>Hf-MOF-808</th>
<th>Hf-MOF-808-PO₄</th>
<th>Hf-MOF-808-SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-nitroaniline</td>
<td>Red / Yellow</td>
<td>–0.2</td>
<td>–</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>Yellow / Colorless</td>
<td>–8.1</td>
<td>–</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>2,4-dinitrotoluene</td>
<td>Yellow / Colorless</td>
<td>–13.8</td>
<td>–</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Next, the potentiometric acid–base titration method was used to estimate the surface acidity of the synthesized MOFs in aqueous solution. This technique was employed to understand the surface property, including surface acidity and topology, of porous materials such as silica and zeolites, and MOFs$^{9-11}$. Before titration, the pH values of aqueous suspensions of MOFs$^{12-13}$ were roughly estimated as 4.07 (Hf-MOF-808), 3.60 (Hf-MOF-808-PO₄), and 3.30 (Hf-MOF-808-SO₄), respectively, suggesting the acidity of MOFs are $\text{Hf-MOF-808-SO}_4 > \text{Hf-MOF-808-PO}_4 > \text{Hf-MOF-808}$. Acid–base titration of activated Hf-MOF-808 reveals four distinct equivalence points at 2.41, 3.22, 3.72, and 5.47 (Figure. S7a and S8a), corresponding to $pK_a$ values of 3.00, 5.61, 8.13, and 9.36, respectively. This result is consistent with the previous report for Zr₆-node MOF808, where four distinct equivalence points with the $pK_a$ values of 3.64, 6.22, 8.23, and 9.12 were reported. Their first three $pK_a$ values can be assigned as those from $\mu_3$-OH, M–OH₂, and M–OH protons ($M = \text{Zr, or Hf}$) of M₆-cluster node (Figure S8d). The fourth $pK_a$ value at higher $pH$ (~10) was unknown and as yet unassigned.$^{11}$ The stronger acidity of Hf-MOF-808, especially for those from $\mu_3$-OH, M–OH₂ protons, compared to the reported Zr₆-node MOF-808 would be because the Hf₆-node nature$^{11}$ and maybe because formate ions (synthetic modulator) were not completely removed from the node in the reported MOF-808 sample. As shown in Figures S7b and S7c, Acid–base titration of activated Hf-MOF-808-PO₄ and Hf-MOF-808-SO₄ displayed different trends with
the emergence large peak at low pH region in the first derivatives of the titration curves, indicating the changes of the surface acidities and topologies compared to that of Hf-MOF-808. In case of Hf-MOF-808-PO₄, the several peaks exist after the initial peak. Here, six Lorentzian functions were employed for the curve-fitting analyses, which suggested of the equivalence points at 2.13, 2.26, 3.07, 3.99, 4.45 and 5.04 (Figures S7b and S7b), resulting in pKₐ values at 2.85 (µ₃-OH), 6.00 (Hf–OH₂), 7.74 (Hf–OH), 8.58, 9.16 and 9.89, respectively. Meanwhile, Hf-MOF808-SO₄ reveals six distinct equivalence points at 1.74, 2.63, 2.85, 3.00, 4.32, and 5.00 (Figures. S7c and S8c), corresponding to pKₐ values of 2.85 (µ₃-OH), 5.34 (Hf–OH₂), 6.76 (Hf–OH₂), 7.53 (Hf–OH), 9.03 and 10.2, respectively. For both Hf-MOF-808-PO₄ and Hf-MOF-808-SO₄, stabilization of protons of µ₃-OH was suggested. Their large difference in the pH regions of Hf–OH₂ and Hf–OH protons might be explained from the difference in their bond natures, i.e., the difference in the interaction between protons and the single-bonded P–O or the double-bonded S=O.
Supporting Figure S7. Potentiometric acid–base titration tests of (a) Hf-MOF-808, (b) Hf-MOF-808-PO₄, and (c) Hf-MOF-808-SO₄. The red and gray curves represent the titration curve and its first derivative curve, respectively. $V_{\text{NaOH}} =$ the total volume of 0.1 M NaOH
Supporting Figure S8. Curve fittings for the first derivatives of the titration curves of (a) Hf-MOF-808, (b) Hf-MOF-808-PO₄, and (c) Hf-MOF-808-SO₄. The gray triangles, the black dotted curves, and the red curves represent the experimental first derivatives (dPH/dV) points, fitting curves, and the sum of the fitting curves, respectively. The peaks were fitted using the sum of Lorentzian functions. (d) A schematic figure of Brønsted acid sites on Hf₆-node. μ₃-OH, Hf-OH₂, and Hf-OH protons are illustrated in red, blue, and green colors, respectively.
2-2. Syntheses and characterization of Pd-SIM MOFs

2-2-1. Pd-SIM

\textbf{Pd@Hf-MOF-808.} Roughly 50 mg of Hf-MOF-808 was solvent exchanged with acetone for two days, and then solvent exchanged with dichloromethane (DCM) for two days. Then, the sample was immersed in 12 mL of 15 mM Pd(OAc)$_2$ solution of DCM for 1 day, and then washed by fresh DCM. Dark brown colored powder was obtained (Figure S9b). ICP measurement showed 2.4 Pd atoms per one Hf$_6$-node.

\textbf{Pd@Hf-MOF-808-PO$_4$.} Roughly 50 mg of Hf-MOF-808-PO$_4$ was solvent exchanged with acetone for two days, and then solvent exchanged with DCM for two days. Then, the sample was immersed in 12 mL of 15 mM Pd(OAc)$_2$ solution of DCM for 1 day, and then washed by fresh DCM. Yellow–light brown colored powder was obtained (Figure S9c). ICP measurement showed 2.2 Pd atoms per one Hf$_6$-node.

\textbf{Pd@MOF-808-SO$_4$.} Roughly 50 mg of Hf-MOF-808-SO$_4$ was solvent exchanged with acetone for two days, and then solvent exchanged with DCM for two days. Then, the sample was immersed in 12 mL of 15 mM Pd(OAc)$_2$ solution of DCM for 1 day, and then washed by fresh DCM. Yellow–light brown colored powder was obtained (Figure S9d). ICP measurement showed 2.3 Pd atoms per one Hf$_6$-node.
Supporting Figure S9. Photos of Pd-SIM Hf-MOF-808 samples. (a) Hf-MOF-808 (white color) (b) Pd@Hf-MOF-808 (reddish brown–dark brown color) (c) Pd@Hf-MOF-808-PO$_4^-$ (yellow–light brown color) (d) Pd@Hf-MOF-808-SO$_4^-$ (yellow–light brown color)

Supporting Figure S10. TEM images for Pd@Hf-MOF-808-Pd. Large crystals (~25 µm) of Pd@Hf-MOF-808 were isolated by sonication in DCM prior to TEM observation, which also causes Pd nanoparticle formation.

Table S3. The Pd(II) precursor concentration and the amount (per Hf$_6$-node) of incorporated Pd (Pd amount was determined by ICP)

<table>
<thead>
<tr>
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<th>Pd precursor concentration / mM (in DCM)</th>
</tr>
</thead>
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</tr>
<tr>
<td>Pd@Hf-MOF-808</td>
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</tr>
<tr>
<td>Pd@Hf-MOF-808-PO$_4^-$</td>
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<tr>
<td>Pd@Hf-MOF-808-SO$_4^-$</td>
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</tbody>
</table>
Supporting Figure S11. TGA curves of (a) Pd@Hf-MOF-808, (b) Pd@Hf-MOF-808-PO₄, and (c) Pd@Hf-MOF-808-SO₄. The first weight loss was observed at approximately 100 °C due to the desorption of H₂O or solvents. Between 100 and 200 °C, the second weight loss was observed, which could be attributed to the loss of the node water. Above 230 °C, the second weight loss was observed, which could be attributed to the loss of the node water. And above 450 °C, the third weight loss due to the loss of trimesic acid were observed.
2-2-2. XPS characterization

Supporting Figure S12. XPS spectra of Hf 4f region. (a), (c), (e) Hf 4f\textsubscript{7/2} and 4f\textsubscript{5/2} core-level spectra of Pd@Hf-MOF-808, Pd@Hf-MOF-808-PO\textsubscript{4}, and Pd@Hf-MOF-808-SO\textsubscript{4} with various Pd amount. (b), (d), (f) XPS spectra and the fitting result for Pd@Hf-MOF-808, Hf-MOF-808-PO\textsubscript{4}, and Pd@Hf-MOF-808-SO\textsubscript{4}. obsd = observed
2-2-3. Raman Spectra

Supporting Figure S13. Raman spectra (632.8 nm excitation, rt) of (a) Hf-MOF-808 and Pd@Hf-MOF-808 (b) Hf-MOF-808-PO₄ and Pd@Hf-MOF-808-PO₄ (c) Hf-MOF-808-SO₄ and Pd@Hf-MOF-808-SO₄. The broad peak at approximately 1050 and 1180 cm⁻¹ could be assigned to the P=O and S=O stretching modes of coordinated phosphoric and sulfuric acid in Hf-MOF-808-SO₄, and Hf-MOF-808-PO₄, respectively. The sharp peak at approximately 1000 cm⁻¹ could be associated to the C=C symmetric ring breathing modes of the BTC ligand, and the relatively sharp peaks at approximately 800 and 200 cm⁻¹ is assigned as O-H bending and Hf-μ₃O asymmetric stretching mode of the Hf₆-node. The small sharp peak at 950 cm⁻¹ appeared after Pd-SIM would probably come from C–C stretching vibration mode of acetate.
2-2-4. Single-crystal X-ray Diffraction Analyses after Pd-SIM

Supporting Figure S14. Microscopic pictures of (a) Hf-MOF-808 (b) Pd@Hf-MOF-808 (c) Pd@Hf-MOF-808-PO₄, and (d) Pd@Hf-MOF-808-SO₄.
Supporting Figure S15. The node structure of Pd@Hf-MOF-808. (a) and (b) top and side view of the node structure. Both acetate (C4 and C5) and palladium (Pd1) were observed on the node. Their occupancy levels were set as 15% and 7.5%, corresponding to 0.9 acetate and 0.9 palladium per Hf₆-node. (c) A $F_o - F_c$ contoured Fourier map of Pd@Hf-MOF-808 in the plane containing Hf1, Hf1*, and O3 of (b). The 2D contoured map was calculated from Pd / acetate omitted crystallographic information file using Platon software. The contours are from $-1.40$ to $1.40 \, \text{e} \, \text{Å}^{-3}$ in step of $0.2 \, \text{e} \, \text{Å}^{-3}$. (d) and (e) The contour maps shifted 0.3 and 0.6 Å perpendicular to the plane of (c). The electron densities from acetate and coordinated palladium were clearly visualized.
Supporting Figure S16. $F_o - F_c$ contoured Fourier maps of Pd@Hf-MOF-808 (a and b), Pd@Hf-MOF-808-PO$_4$ (c and d), Pd@Hf-MOF-808-SO$_4$ (e and f). The 3D contoured maps were calculated from Pd omitted crystallographic information file using SHEXL software. The contours are from $-0.80$ to $0.80$ e Å$^{-3}$ for Pd@Hf-MOF-808, from $-0.70$ to $0.70$ e Å$^{-3}$ for Pd@Hf-MOF-808-PO$_4$, and from $-0.60$ to $0.60$ e Å$^{-3}$ for Pd@Hf-MOF-808-SO$_4$, respectively. The relatively strong electron densities which would come from the coordinated palladium were visualized for Pd@Hf-MOF-808 and Pd@Hf-MOF-808-PO$_4$. For Pd@Hf-MOF-808, acetate ions were also suggested to coordinate on the node. Here, the crystallographically determined Pd amount (0.9 Pd per Hf$_6$-node) is less than half of the ICP result (2.2 Pd per Hf$_6$-node), indicating the existence of other disordered Pd sites with small occupancies. In the case of Pd@Hf-MOF-808-SO$_4$, the Pd(II) sites could not be determined via SCXRD measurements even though several single-crystals were surveyed.
Supplementary Table S4 | Crystallographic data of Pd-SIM MOFs

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<td>C_{18}H_{6}O_{32}Hf_{6}(PdC_{4})_{0.90}</td>
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2-2-5. Stability Tests of Incorporated Pd(II) under H₂

Stability tests of Pd(II) sites under H₂ atmosphere were investigated using the following procedure. ca. 5 mg of Pd-SIM MOF samples were added to a Microwave vial (Biotage, 10 mL) and sealed. The Hydrogen gas (100% H₂ or 2% H₂ and 98% N₂) was purged in the vial for 1 min and then connected to an balloon containing the hydrogen gas. XPS measurements were performed after 1 h for 100% H₂ gas or 12h for 2% H₂ gas. The XPS measurements results were summarized in Table S5 and Figure S17.

Supporting Table S5. Pd(II) : Pd (0) ratio after H₂ treatment. The ratio was calculated from the integrated area ratio of XPS Pd 3d5/2 region in Figure S6.

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<th>2% H₂, rt 12h</th>
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<tr>
<td>Pd@Hf-MOF-808-SO₄</td>
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Supporting Figure S17. XPS spectra (Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ core-level region) after H$_2$ treatment. (a), (c), and (e) the spectra of Pd@Hf-MOF-808, Pd@Hf-MOF-808-PO$_4$, Pd@Hf-MOF-808-SO$_4$ after sitting under 100% H$_2$ atmosphere for 1 h. (b), (d), and (f) the spectra of Pd@Hf-MOF-808, Pd@Hf-MOF-808-PO$_4$, Pd@Hf-MOF-808-SO$_4$ after sitting under 2% H$_2$ atmosphere (98% N$_2$) for 12 h.
2-2-6. Catalytic Test Reactions

To a 10 mL Biotage microwave vial, 2-phenylphenol (1; 42.5 mg, 0.25 mmol), ethyl acrylate (264 μL, 2.5 mmol), copper(II) acetate monohydrate (4 mg, 0.02 mmol), triethylamine (70 μL, 0.54 mmol), mesitylene (internal standard: 20 μL, 0.14 mmol), Pd catalyst (0.050 mmol of Pd), and 2-methylbutanol (1 mL) were added and sealed. The system was purged under O₂ for 1 min and connected to an oxygen balloon, and then heated at 105 °C under mechanical stirring. ~0.1 mL of the reaction mixture was removed from the system at intervals of a few hours after heating using a 1 mL syringe. The reaction mixture was diluted with 1 mL of acetone, and insoluble solids were removed by centrifuge. The conversion was determined by the GC. Standards with given concentrations of substrate and product, namely, 1 and 2, were prepared. Using the area ratio vs. the mol ratio of the compounds and the internal standard (mesitylene), calibration curves of each compound were generated. Here, the pure reaction product 2 for the GC standard was obtained by the purification of the combined reaction mixtures using a flash column chromatography on silica gel using hexane/ethyl acetate (2:1 mixture) as the eluent. The NMR spectra of 2 was shown in Figure S19.
Supporting Figure S18. The proposed reaction mechanism of the formation of 2
Supporting Figure S19. NMR spectra of the reaction product 2 (400 MHz, CDCl₃ solvent). (a) Full spectrum. The chemical structure of the product was also shown. The peaks (*) at 0.89 and 1.27 ppm come from hexane, and the peaks (*) at 1.23, 2.00, and 4.08 come from ethyl acetate. (b) The magnified spectrum of the aromatic region. The singlet peak at 7.26 ppm is the residual solvent signal. ¹H NMR: δ 1.23 (H₆; 3H, t, J = 7.2 Hz), 2.60-2.90 (H₅; 2H, (2.64, 0.4H, d, J = 5.2 Hz), (2.68, 0.6H, d, J = 5.2 Hz), (2.90, 0.6H, d, J = 8.8 Hz), (2.94, 0.4H, d, J = 8.4 Hz)), 4.15 (H₇; q, J = 7.2 Hz)), 5.66 (H₄; 1H, dd, J = 5.2, 8.8 Hz), 6.93 (H₃; 1H, dd, J = 8.0, 1.2 Hz), 7.02 (H₈; 1H, td, J = 8.0, 1.2 Hz), 7.13 (H₉; 1H, dd, J = 8.0 Hz), 7.20 (H₁₀; 1H, m, J = 8.0, 1.6 Hz), 7.25 (H₁₁; 1H, td, J = 8.0, 1.2 Hz), 7.34 (H₁₂; 1H, td, J = 8.0, 1.2 Hz), 7.68 (H₁₃; 1H, m, J = 8.0, 1.2 Hz), 7.69 (H₁₄; 1H, dd, J = 8.0, 1.6 Hz).
Supporting Figure S20. PXRD patterns after catalytic tests of (a) Pd@Hf-MOF-808 (b) Pd@Hf-MOF-808-PO₄ (c) Pd@Hf-MOF-808-SO₄
Supporting Figure S21. XPS spectra (Pd 3d_{5/2} and Pd 3d_{3/2} core-level region) of (a) Pd@Hf-MOF-808 (b) Pd@Hf-MOF-808-PO₄ (c) Pd@Hf-MOF-808-SO₄
3. Computational Characterization

3-1. Computational Method

All density functional calculations were carried out using the M06-L density functional implemented in Gaussian 09. The def2-SVP basis set was employed for H, C, and O atoms, the def2-TZVP basis set was employed for P and S atoms, and the def2-TZVPP basis set was employed for Hf and Pd atoms with the SDD effective core potential for Hf and Pd atoms. In all cases, the positions of all atoms were optimized in the gas phase, except for the C atoms of the capping benzoate groups, which were fixed at their positions in an optimized structure of Hf-MOF-808. Zero-point energies and thermal contributions to enthalpies and Gibbs free energies were derived from vibrational frequency calculations performed at the same level of theory at 298.15 K and 1 atm. We verified that none of the stationary points have imaginary frequencies. Free energies of solvation in dichloromethane (DCM) solvent were calculated by performing single-point energy calculations at the gas-phase geometries using the SMD solvation model, and the relative solution-phase Gibbs free energies were calculated by adding the free energies of solvation to the gas-phase relative Gibbs free energies.

The Cartesian coordinates of all the structures and their associated electronic energies, enthalpies, and Gibbs free energies in the gas phase and their free energies in solution (solvent: DCM) are given in the Supporting Information. The energy values reported in the main text are Gibbs free energies (298.15 K, standard state of 1 atm for gases and 1 M for solutes) in DCM.
3-2. Computational Models

**Hf-MOF-808 cluster model.** The Hf₆ node of Hf-MOF-808 was truncated from an optimized periodic structure of Hf-MOF-808 by replacing the organic linkers by benzoate groups Figure S22(a). The Hf-MOF-808 cluster model is composed of Hf₆(μ₃-O)₄(μ₃-OH)₄(H₂O)₆(OH)₆ nodes shown in Figure S22(b) and six benzoate linkers shown in Figure S22(c).

![Figure S22](image)

**Supporting Figure S22.** The structure of (a) Hf₆ node [Hf₆(μ₃-O)₄(μ₃-OH)₄], (b) Hf₆ node with 6 pairs of OH and H₂O groups [Hf₆(μ₃-O)₄(μ₃-OH)₄(H₂O)₆(OH)₆], and (c) Hf₆ node with 6 benzoate linkers. The atoms on the front side are black, and those on the back side are grey.
**Hf-MOF-808-PO₄/SO₄ cluster models.** The OH and H₂O ligands shown in Figure S22(b) can react with H₃PO₄ or H₂SO₄, and in this way one can deposit acidic functional groups on the node. The deposition processes are:

\[
\text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_6(OH)_6 + 2 \text{H}_3\text{PO}_4
\rightarrow \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(H_2\text{PO}_4)_2 + 4\text{H}_2\text{O}
\] (1)

\[
\text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_6(OH)_6 + 2 \text{H}_2\text{PO}_4
\rightarrow \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(\text{HSO}_4)_2 + 4\text{H}_2\text{O}
\] (2)

Here, we considered two acidic groups per Hf₆ node because the ICP-OES measurements indicated 2.4 phosphorous and 2.4 sulfur atoms per Hf₆-node for Hf-MOF-808-PO₄ and Hf-MOF-808-SO₄, respectively. Each acidic group (H₂PO₄ or HSO₄) replaces one H₂O and one OH group on different Hf ions, and therefore it bridges two Hf ions. For example, removing the H₂O coordinated at Hf₁, the H₂O and OH group coordinated at Hf₂, and the OH group at Hf₅ opens two bridging sites on the Hf₆ node, namely Hf₁-Hf₂ and Hf₂-Hf₅, and this generates the structure called PO₄-1,2-2,5 in Figure S23, denoted as PO₄-1,2-2,5. We also tested the tautomer of PO₄-1,2-2,5 generated by moving the proton of H₂PO₄⁻ to the node; this structure is denoted as PO₄-1,2-2,5-A in Figure S23. We have identified all the possible structures of Hf-MOF-808-PO₄ that can be generated in the above way without transferring a proton, and in Figure S23 we show these structures and a selection of tautomers obtained by moving a proton. The structures are labeled as PO₄-k,l-m,n, where k, l are the attachment Hf atoms of the first acidic group, m, n are the attachment Hf atoms of the second acidic group, and their tautomers are labeled as PO₄-k,l-m,n-A or PO₄-k,l-m,n-B.
Pd(II)@Hf-MOF-808, Pd(II)@Hf-MOF-808-PO4, and Pd(II)@Hf-MOF-808-SO4 cluster models. The deposition of Pd(II) involves Pd(OAc)2 reacting with the proton of a ligand or a OH ligand, H2PO4 or HSO4 acidic functional groups. The deposition processes are:

\[ \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_6(OH)_6 + \text{Pd(OAc)}_2 \rightarrow \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_5(OH)_7(\text{PdOAc}) + \text{HOAc} \] (3)

\[ \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(H_2PO_4)_2 + \text{Pd(OAc)}_2 \rightarrow \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(H_2PO_4)(HPO_4)(\text{PdOAc}) + \text{HOAc} \] (4)

\[ \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(HSO_4)_2 + \text{Pd(OAc)}_2 \rightarrow \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(HSO_4)(SO_4)(\text{PdOAc}) + \text{HOAc} \] (5)

The Pd(II)@Hf-MOF-808 cluster models are created by removing one proton from an H2O group and then bridging or chelating PdOAc between two O atoms of terminal OH groups. The structures are denoted as Pd(II)@H2O-k,l, where k and l are the attachment Hf atoms of the OH and H2O groups.

The Pd(II)@Hf-MOF-808-PO4/SO4 cluster models are created by first removing one proton from an H2PO4 group, an HSO4 group, or an H2O group and then bridging PdOAc between two O atoms. We distinguish three different kinds of O atoms:

- **t** ("terminal") represents an O atom of a terminal H2O or OH on the node;
- **o** ("outer") represents an O atom that is part of a PO4 group but that is not bonded to a Hf ion;
- **i** ("inner") represents an O atom that is part of a PO4 group and that is also bonded to a Hf ion.

The structures are labeled as Pd(II)@PO4-k,l-m,n-uxwy, where k,l-m,n are the same as in Figure S23, u and w denote the type (t, o, or i) of the attachment O atoms, and x and y are the attachment Hf atoms of the PO4, H2O, and OH groups. The tautomers are labeled as Pd(II)@PO4-k,l-m,n-uxwy-A or Pd(II)@PO4-k,l-m,n-uxwy-B.
Pd(0)@Hf-MOF-808, Pd(0)@Hf-MOF-808-PO₄, and Pd(0)@Hf-MOF-808-SO₄ cluster models. The binding of Pd(0) are created by deposition of one Pd atom on Hf-MOF-808, Hf-MOF-808-PO₄ or Hf-MOF-808-SO₄. The deposition processes are:

\[
\text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_6(OH)_6 + \text{Pd}(0) \\
\rightarrow \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_6(OH)_6\text{Pd}(0) \quad (6)
\]

\[
\text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(H_2PO_4)_2 + \text{Pd}(0) \\
\rightarrow \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(H_2PO_4)_2\text{Pd}(0) \quad (7)
\]

\[
\text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(HSO_4)_2 + \text{Pd}(0) \\
\rightarrow \text{Hf}_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4(HSO_4)_2 \text{Pd}(0) \quad (8)
\]

The energy of Pd(0) was calculated from an isolated singlet Pd atom.
3-3. Computational Results

Supporting Figure S23. The structures of Hf-MOF-808-PO_4 with their relative solution-phase Gibbs free energies, $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes).
**Supporting Figure S24 (in the previous page).** The structures of Pd(II)@Hf-MOF-808-PO₄ with their relative Gibbs free energies $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.

Supporting Figure S25. The structures of Pd(0)@Hf-MOF-808-PO₄ with their relative Gibbs free energies $\Delta G^\circ$ (kcal/mol), (298.15 K, standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.
Supporting Figure S26. The reaction network for the formation of Pd(II)@Hf-MOF-808 and Pd(0)@Hf-MOF-808 with their Gibbs free energies of reactions $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.
Supporting Figure S27. The structures of Hf-MOF-808-SO4 with their relative Gibbs free energies $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.
Supporting Figure S28. The structures of Pd(II)@Hf-MOF-808-SO₄ with their relative Gibbs free energies $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.
Supporting Figure S29. The structures of Pd(II)@Hf-MOF-808-SO₄ with their relative Gibbs free energies $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.
Supporting Figure S30 (in the previous page). The reaction network for the formation of Pd(II)@Hf-MOF-808-SO₄ and Pd(0)@Hf-MOF-808-SO₄ with their Gibbs free energies of reactions $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.

![Reaction Diagrams]

$\Delta G = -2.1$

$\Delta G = -2.9$

$\Delta G = 0.0$

Supporting Figure S31. The structures of Pd(0)@Hf-MOF-808 with their relative Gibbs free energies $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.
Supporting Figure S32. The reaction network for the formation of Pd(II)@Hf-MOF-808 and Pd(0)@Hf-MOF-808 with their Gibbs free energies of reactions $\Delta G^\circ$ (kcal/mol at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes) including the solvation effect of DCM.
**Supporting Table S6.** The electronic energies \((E(g))\), enthalpies \((H(g), 298.15 \text{ K})\), and Gibbs free energies \((G(g), 298.15 \text{ K})\) of all the possible structures of Hf-MOF-808-PO\(_4\) after optimization in the gas phase and the electronic energies \((U(\text{sol}))\) of single-point energy calculations at the gas-phase geometries including the solvation free energy in DCM as obtained by the SMD solvation model

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<th>(G(g)) /a.u.</th>
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<td>PO(_4)-2,5-3,5</td>
<td>-5308.863196</td>
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<tr>
<td>PO(_4)-2,5-3,5-A</td>
<td>-5308.854947</td>
<td>-5308.070776</td>
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<td>-5308.934919</td>
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</tbody>
</table>
**Supporting Table S7.** The electronic energies \((E(g))\), enthalpies \((H(g), 298.15 \text{ K})\), and Gibbs free energies \((G(g), 298.15 \text{ K})\) of all the possible structures of \(\text{Pd(II)}@\text{Hf-MOF-808-PO}_4\) after optimization in the gas phase and the electronic energies \((U(\text{sol}))\) of single-point energy calculations at the gas-phase geometries including the solvation free energy in DCM as obtained by the SMD solvation model.

<table>
<thead>
<tr>
<th>Structures</th>
<th>(E(g)) /a.u.</th>
<th>(H(g)) /a.u.</th>
<th>(G(g)) /a.u.</th>
<th>(U(\text{sol})) /a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pd(II)}@\text{PO}_4-1,2-2,5-i2i2)</td>
<td>-5664.568067</td>
<td>-5663.737213</td>
<td>-5663.892680</td>
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<tr>
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<td>-5664.668055</td>
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<tr>
<td>(\text{Pd(II)}@\text{PO}_4-1,2-2,5-i2i2-B)</td>
<td>-5664.602182</td>
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<td>(\text{Pd(II)}@\text{PO}_4-1,2-2,5-o2o2-A)</td>
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Supporting Table S8. The electronic energies ($E(g)$), enthalpies ($H(g)$, 298.15 K), and Gibbs free energies ($G(g)$, 298.15 K) of all the possible structures of Pd(0)@Hf-MOF-808-PO$_4$ after optimization in the gas phase and the electronic energies ($U$(sol)) of single-point energy calculations at the gas-phase geometries including the solvation free energy in DCM as obtained by the SMD solvation model

<table>
<thead>
<tr>
<th>Structures</th>
<th>$E(g)$ /a.u.</th>
<th>$H(g)$ /a.u.</th>
<th>$G(g)$ /a.u.</th>
<th>$U$(sol) /a.u.</th>
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<tr>
<td>Pd(0)@PO$_4$-2,5-3,5-A</td>
<td>-5436.861082</td>
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<td>Pd(0)@PO$_4$-2,5-3,5-B</td>
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<td>-5436.224228</td>
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<tr>
<td>Pd(0)@PO$_4$-2,5-3,5-C</td>
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<td>-5436.087337</td>
<td>-5436.235716</td>
<td>-5436.952532</td>
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Supporting Table S9. The electronic energies \((E(g))\), enthalpies \((H(g), 298.15 \text{ K})\), and Gibbs free energies \((G(g), 298.15 \text{ K})\) of all the possible structures of Hf-MOF-808-SO₄ after optimization in the gas phase and the electronic energies \((U(\text{sol}))\) of single-point energy calculations at the gas-phase geometries including the solvation free energy in DCM as obtained by the SMD solvation model.

<table>
<thead>
<tr>
<th>Structures</th>
<th>(E(\text{g})/\text{a.u.})</th>
<th>(H(\text{g})/\text{a.u.})</th>
<th>(G(\text{g})/\text{a.u.})</th>
<th>(U(\text{sol})/\text{a.u.})</th>
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<tbody>
<tr>
<td>SO₄-1,2-3,4-A</td>
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<td>-5421.12839</td>
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<td>SO₄-1,2-4,6-A</td>
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Supporting Table S10. The electronic energies ($E(g)$), enthalpies ($H(g)$, 298.15 K), and Gibbs free energies ($G(g)$, 298.15 K) of all the possible structures of Pd(II)@Hf-MOF-808-SO$_4$ after optimization in the gas phase and the electronic energies ($U$(sol)) of single-point energy calculations at the gas-phase geometries including the solvation free energy in DCM as obtained by the SMD solvation model

<table>
<thead>
<tr>
<th>Structures</th>
<th>$E(g)$ /a.u.</th>
<th>$H(g)$ /a.u.</th>
<th>$G(g)$ /a.u.</th>
<th>$U$(sol) /a.u.</th>
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</thead>
<tbody>
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<tr>
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<td>Pd(II)@SO$_4$-1,2-4,6-o1o2</td>
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<td>-5775.976638</td>
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Supporting Table S11. The electronic energies ($E(g)$), enthalpies ($H(g)$, 298.15 K), and Gibbs free energies ($G(g)$, 298.15 K) of all the possible structures of Pd(0)@Hf-MOF-808-SO$_4$ after optimization in the gas phase and the electronic energies ($U$(sol)) of single-point energy calculations at the gas-phase geometries including the solvation free energy in DCM as obtained by the SMD solvation model

<table>
<thead>
<tr>
<th>Structures</th>
<th>$E(g)$ /a.u.</th>
<th>$H(g)$ /a.u.</th>
<th>$G(g)$ /a.u.</th>
<th>$U$(sol) /a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(0)@SO$_4$-1,2-3,4-o3o4</td>
<td>-5549.068</td>
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</table>

Supporting Table S12. The solution-phase 298.15 Gibbs free energy for the deposition of Pd(OAc)$_2$ or Pd atom on Hf-MOF-808, Hf-MOF-808-SO$_4$, and Hf-MOF-808-PO$_4$:

<table>
<thead>
<tr>
<th>$\Delta G$ (kcal/mol)</th>
<th>Hf-MOF-808</th>
<th>Hf-MOF-808-SO$_4$</th>
<th>Hf-MOF-808-PO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(II)</td>
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<td>-4.0</td>
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<td>-36.4</td>
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</tbody>
</table>

$^a$ The Gibbs free energies of reactions $\Delta G$ (kcal/mol) are calculated at 298.15 K, with a standard state of 1 atm for gases and 1 M for solutes including the solvent effect of DCM.
### Supporting Table S13. A comparison of supported Pd catalysts for oxidative Heck reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction</th>
<th>Catalyst Support</th>
<th>Reaction Condition</th>
<th>TOF (h⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| 1      | ![Ph-B-O + nHex → Ph-C-nHex](image) | CMP-1 | 40 °C  
1 bar O₂  
Cu(O Tf)₂ (20 mol%)  
DMA | N. A. | 23 |
| 2      | ![Ph → PDMS](image) | PDMS | 120 °C  
8 bar O₂  
CF₃SO₃H (5.33 mol%)  
AcOH/H₂O | 91 | 24 |
| 3      | ![Ph-N + ZrO₂](image) | ZrO₂ | 100 °C  
2.5 bar O₂  
AcOH-dioxane (1:1) | N. A. | 25 |
| 4      | ![Ph → UiO-67-bipy](image) | UiO-67-bipy;  
UiO-66-COOH;  
MOF-808;  
UMCM-309a;  
UiO-66;  
ZrO₂ | 90 °C  
16 bar O₂  
1-PrSO₃H (0.5 mol%)  
AcOH | 1.1 (UiO-67-bipy);  
10.6 (UiO-66-COOH);  
11.2 (MOF-808);  
11.1 (UMCM-309a);  
8.3 (UiO-66);  
10.5 (ZrO₂) | 26 |
| 5      | ![OH- + nHex → Hf-MOF-808-SO₄](image) | Hf-MOF-808;  
Hf-MOF-808-SO₄;  
Hf-MOF-808-PO₄ | 105 °C  
1 bar O₂  
2-methyl-1-butanol | 0.06 (Hf-MOF-808);  
0.33 (Hf-MOF-808-SO₄);  
0.93 (Hf-MOF-808-PO₄) | This work |
5. Supporting References


