

1 Rational Approach to Guest Confinement inside MOF Cavities for Low-

2 Temperature Catalysis

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29 **Abstract:**

30 Geometric or electronic confinement of guests inside nanoporous hosts promises to deliver
31 unusual catalytic or opto-electronic functionality from existing materials but is challenging to
32 obtain particularly using metastable hosts, such as metal-organic frameworks (MOFs).
33 Reagents (e.g. precursor) may be too large for impregnation and synthesis conditions may
34 also destroy the hosts. Here we use thermodynamic Pourbaix diagrams (favorable redox and
35 pH conditions) to describe a general method for metal-compound guest synthesis by
36 rationally selecting reaction agents and conditions. Specifically we demonstrate a MOF-
37 confined RuO₂ (RuO₂@MOF-808-P) RuO₂@MOF-808-P with exceptionally high catalytic
38 CO oxidation below 150 °C as compared to the conventionally made SiO₂-supported RuO₂
39 (RuO₂/SiO₂). This can be caused by weaker interactions between CO/O and the MOF-
40 encapsulated RuO₂ surface thus avoiding adsorption-induced catalytic surface passivation.
41 We further describe applications of the Pourbaix-enabled guest synthesis (PEGS) strategy
42 with tutorial examples for the general synthesis of arbitrary guests (e.g. metals, oxides,
43 hydroxides, sulfides).

44 **Introduction**

45 Loading guests (e.g. molecules, clusters or particles) inside the pre-existing pores of
46 nanoporous hosts (guest@nanoporous-host) is one of the key post-synthesis modification
47 strategies for porous materials.¹⁻¹⁷ It can yield highly active and stable heterogeneous
48 catalysts^{2-4,9-17} as well as robust photo/electro-luminescence materials^{2,5,6,18} with tunable
49 band structures in quantum confinement. Forming guests within the pores has been
50 extensively explored using inorganic nanoporous materials^{1,2,10} and supramolecular cages^{5,11}
51 (i.e. host-guest chemistry and/or inclusion chemistry). Besides metal
52 particles/clusters,^{4,13,14,16,19} however, such synthesis is still challenging or impossible for
53 other types of guest particles/clusters (e.g. oxides, hydroxides, sulfides, nitrides, phosphides)

54 inside the host's cavity/channel. Many hosts have very small aperture (a.k.a. window)
55 opening sizes (typically < 2 nm), so direct impregnation of guest compounds with much
56 larger sizes is no longer feasible. Guests, therefore, have to be assembled locally within the
57 cavity/channel (i.e. ship-in-a-bottle assembly^{9,14,20}). The general 'ship-in-a-bottle' approach is
58 to load smaller precursors (e.g. salts and organometallics) into pre-formed porous host
59 materials via solution-based, gas-phase or mechanical-mixing impregnation, followed by
60 either thermal/photochemical decomposition or redox reaction (with either strong redox
61 reagents, e.g. hydrazine and NaBH_4 , or high-temperature treatment in reducing atmosphere,
62 e.g. H_2).^{2,4} These methods which are useful for bulk or nanostructure synthesis (i.e.
63 unconfined systems) often fail to work properly in nanoporous hosts. The major dilemmas are
64 that (i) many of the reactants are still too large to be impregnated and (ii) the conditions
65 required to form a target guest may damage or destroy the host structure.⁴ Nonetheless, the
66 ship-in-a-bottle strategy has been recently recognized as a promising way to post-
67 synthetically functionalize porous metal-organic frameworks (MOFs),^{3,4,11-17} which are host
68 matrices assembled with metal centers and organic ligands with extremely diverse
69 chemistries, topologies and pore architectures.²¹⁻²⁶ By immobilizing the guests inside MOFs,
70 guest aggregation/fusion can be effectively prevented.^{4,19} Meanwhile, MOF hosts have been
71 found to influence the properties of the guests, e.g. modulation of electron-hole
72 recombination rates for quantum dots.⁴ Hence, there is a demand to carry out ship-in-a-bottle
73 synthesis with sufficiently small reaction reagents under mild conditions, as many of these
74 metastable MOFs suffer from poor chemical and thermal stability.^{2,4,22-25} A rational route for
75 incorporation of guest compounds into an arbitrary nanoporous host should enable the
76 investigation of multiple host-guest systems with surprising functionalities.

77 We realize that the synthetic conditions of guests can be pre-determinable based on
78 pH/potential-dependent equilibrium solid/solution maps²⁷⁻³¹ (well-known by materials

79 scientists as Pourbaix diagrams, e.g. Fig. 1a), which have been extensively investigated and
80 used for depicting relevant thermodynamics during a corrosion process (normally solid $\rightarrow$
81 solution).³² Instead of studying solid $\rightarrow$ solution reactions, we use the Pourbaix diagrams to
82 select precursor solutions and synthetic conditions (i.e. redox potential and/or pH) to solidify
83 the desired guests (i.e. solution $\rightarrow$ solid processes) within the pores of the hosts.³⁰ We term
84 this strategy Pourbaix enabled guest synthesis (PEGS) (Fig. 1a, Supplementary Section 1).
85 Briefly, by checking the Pourbaix diagrams we can find the difference in the redox potential
86 (ΔE) and/or pH between a soluble guest precursor and a desired guest. We can then shortlist
87 the hosts and reagents (e.g. precursors) that meet the guest formation requirements and select
88 the most appropriate candidates perhaps with other properties (i.e. desired boiling
89 temperature and hydrophobicity) to manage the ship-in-a-bottle synthesis.

90 One concern for preparing the ship-in-a-bottle systems is the significant amount of
91 guest depositing outside the hosts,^{4,33} which creates a strong bias against the discovery of new
92 functionalities in confinement.⁶ Efforts to immobilize the precursor and to control the guest
93 formation mostly inside the host include methods such as chemical grafting^{33,34} and
94 electrostatic interactions³⁵. These approaches, however, only work for a small portion of
95 hosts with special chemistries (e.g. hosts with functionalizable parts or electrical charge).
96 Enabled by the PEGS method we may select the desired reagents with functionalities (i.e.
97 temperature-controlled selective desorption and hydrophobic-hydrophilic interaction
98 mentioned in Fig.1 and Supplementary Section 2.4) to control the loading position, thus
99 mitigate the outer-surface deposition issue. Therefore, hosts no longer need to exhibit special
100 chemistries to synthesize the right guests inside them.

101 The ability to synthesize a large variety of catalytic and opto-electronic materials with
102 an even greater variety of available and synthesizable MOF materials is a combinatorial
103 treasure trove of potential discoveries.^{2,4,6,16} We demonstrate the synthesis of RuO₂ confined

104 within a MOF and then characterize the resulting products. The MOF used is MOF-808-P³⁶
105 $[\text{Zr}_6\text{O}_5(\text{OH})_3(\text{BTC})_2(\text{HCOO})_5(\text{H}_2\text{O})_2]$, BTC = 1,3,5-benzenetricarboxylate], which is based on
106 $\{\text{Zr}_6\text{O}_8\}$ clusters (Fig. 1b) with the **spn** topology and has large cavity and aperture diameters
107 (ca. 18 Å and ca. 14 Å, respectively). The MOF is stable in aqueous solution over a wide pH
108 range of 3-10.³⁷ The synthesis of MOF-808-P is modified from MOF-808 and requires
109 shorter time.^{36,38} The good synthetic control of the loaded guests allows us to demonstrate
110 that molecules can behave very differently on the guest surfaces. For example, molecules
111 (such as CO and O₂) adsorbed on the confined RuO₂ at low temperatures (e.g. ≤ 150 °C) can
112 exhibit a drastically different behavior compared with that on porous silica-supported RuO₂.
113 Most surprisingly, such guest inclusion inside the MOF host via PEGS turns inactive oxide
114 surfaces into highly active catalysts. RuO₂, which is usually easily deactivated at low
115 temperatures by strong CO adsorption,³⁹⁻⁴¹ stays highly active in MOF confinement ($> 97\%$
116 conversion after 12 hrs continuous reaction) for CO oxidation. We believe that by using the
117 PEGS method many candidates, e.g. oxide, hydroxide and sulfide materials, can be expected
118 to show other unique and surprising behaviors for catalysis and optoelectronics in
119 confinement. In the following parts we describe in more detail the steps in applying the PEGS
120 approach.

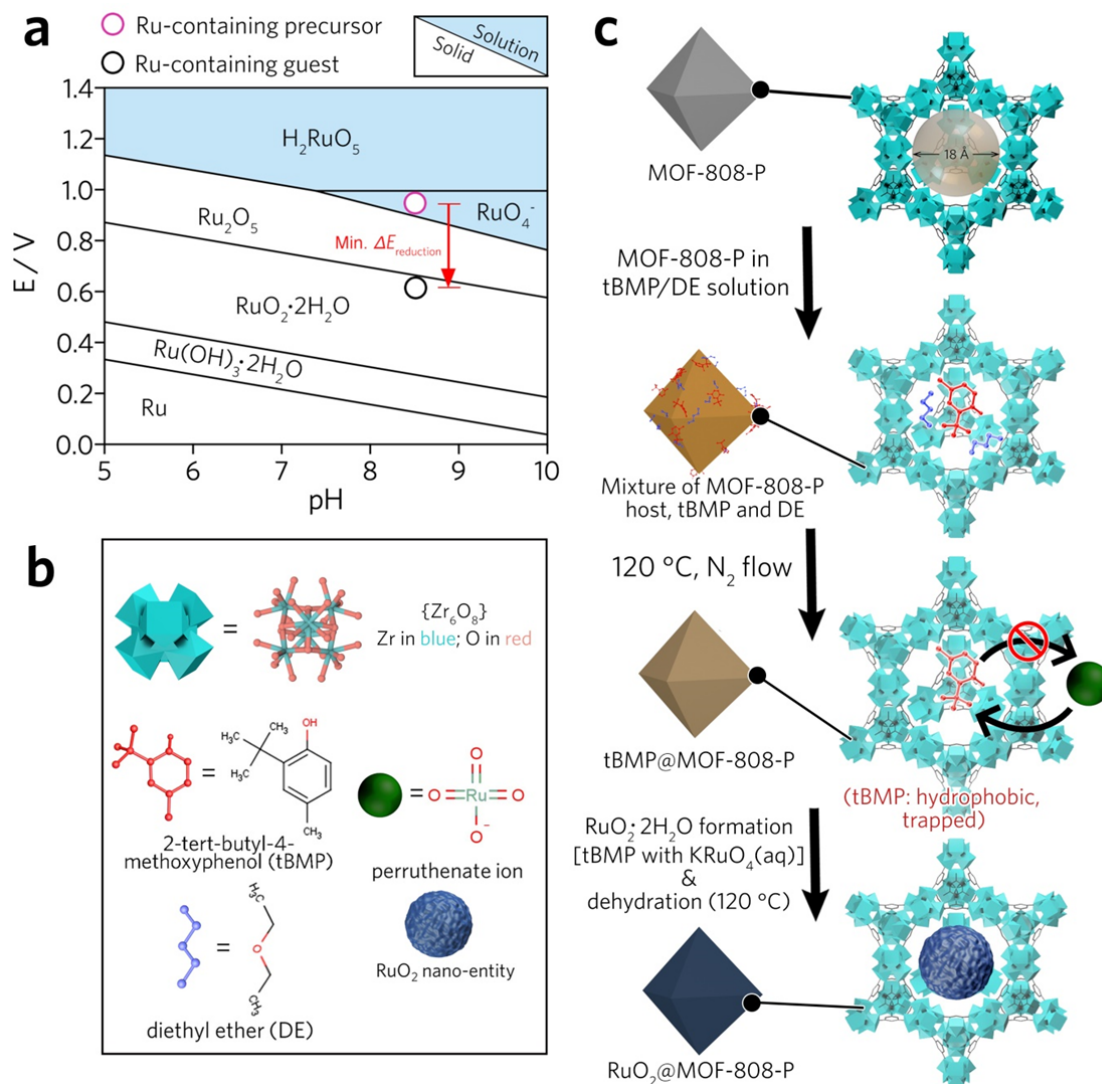


Fig. 1 Pourbaix Enabled Guest Synthesis (PEGS) strategy for RuO₂ incorporation into MOF-808-P. **a** Pourbaix (redox potential-pH) diagram for Ru-H₂O system (with a pH range of 5-10; concentration of Ru-based solution = 20 mM) constructed based on previously available data versus standard hydrogen electrode (SHE).²⁹ Within the pH range it shows the range of potentials where a certain phase is thermodynamically stable, and the potential needed to transform one phase to another, i.e. the red arrow shows that to transform a soluble Ru-based precursor, perruthenate ion (RuO₄⁻), to solid Ru-based guest (i.e. RuO₂·2H₂O) at a pH of ca. 8.5 [20 mM aqueous potassium perruthenate (K₂RuO₄)], one needs minimum reduction potential ($\Delta E_{\text{reduction}}$) of 0.3 - 0.4 V (assuming an unaltered pH). A reductant, such as 2-tert-butyl-4-methylphenol (tBMP) with expected ca. 0.3 V to be oxidized, could

be suitable. Diethyl ether (DE) is used as a solvent for tBMP. **b** shows symbols for the scheme in **c**, which illustrates RuO₂ synthesis inside the cavity of pre-formed MOF-808-P using the hydrophobic reducing lipid tBMP. For clarity, (i) the schematics of MOF-808-P is simplified as standard MOF-808³⁶; (ii) hydrogen atoms and carbon atoms for formates (HCOO⁻) are omitted in the MOF cage.

Results

Rational synthesis of RuO₂ inside MOF-808-P. In revisiting the Pourbaix (redox potential-pH) diagrams of aqueous (element-H₂O) systems²⁷⁻²⁹ (e.g., Ru-H₂O system given in Fig. 1a), we realized that the reverse use of Pourbaix diagrams could guide the formation of insoluble compounds as long as the difference in the redox potentials between the reactants and the pH was chosen to make insoluble cluster formation thermodynamically favorable. For example, oxyanions (A_xO_y^{z-}) in A-H₂O (A) systems could form oxides and hydroxides²⁷⁻²⁹, where A is the desired element in the guest. Therefore, the PEGS strategy that we propose (detailed in Supplementary Section 1 and Supplementary Figure 1) can be more flexible and versatile than known methods^{2,4} and suitable for forming a range of insoluble guest compounds under relatively mild conditions inside pre-formed nanoporous hosts, e.g. MOFs and zeolites. As a demonstration, we have synthesized RuO₂ inside a water-stable Zr-based MOF, MOF-808-P³⁶, i.e. RuO₂@MOF-808-P. We used potassium perruthenate (KRuO₄) as the RuO₂ precursor and 2-tert-butyl-4-methylphenol (tBMP, Fig. 1b) lipid as the reducing agent (Fig. 1; details in Supplementary Section 2.1).

According to the PEGS method tutorial detailed in Supplementary Section 1, from the Ru-H₂O Pourbaix diagram (Fig. 1a) we have seen that at a pH of ca. 8.5 (20 mM aqueous KRuO₄), the minimum $\Delta E_{\text{reduction}}$ required to form RuO₂·2H₂O (the preform of RuO₂) from the RuO₄⁻ (aq) domain is ca. 0.3-0.4 V. Therefore, a small reducing reagent which matches this $\Delta E_{\text{reduction}}$ is required. Additionally, to perform the guest loading with the aforementioned

position control, we need a reducing reagent that is hydrophobic and has temperature-controlled selective desorption capability (Supplementary Section 2.4). We have chosen the small lipid tBMP (Supplementary Figure 2), which meets the above-mentioned properties and is chemically similar to the well-known antioxidant lipid, butylated hydroxytoluene requiring ca. 0.3 V to be partially oxidized.^{42,43} We expect that if it also provides ~0.3 V of oxidation potential, it may be sufficient to reduce RuO_4^- to $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ within a controlled pH range of 5-10.

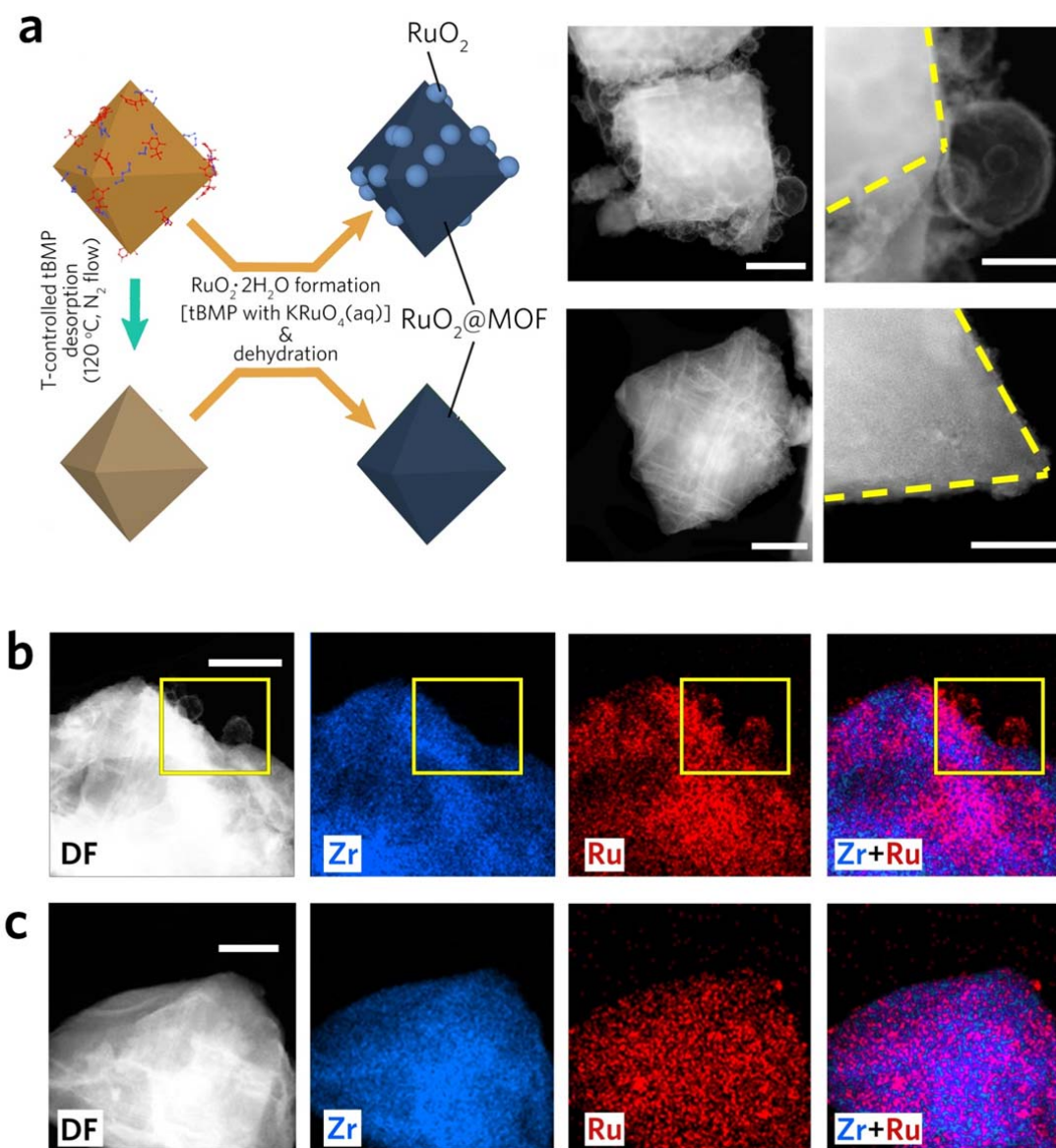
We have verified that the MOF-808-P by itself remains white in color (i.e. no color change) in the KRuO_4 solution, indicating no reaction in the MOF upon placement into the KRuO_4 (aq) solution in the absence of tBMP. For the reaction tBMP is first introduced into the MOF using diethyl ether (DE) as the solvent. With the aid of temperature-controlled selective desorption of tBMP and DE (Supplementary Section 2.4, Supplementary Figure 3),^{8,44} tBMP outside the MOF and all the DE was desorbed, while tBMP inside the MOF mostly remained to obtain tBMP@MOF-808-P. After immersing tBMP@MOF-808-P into the KRuO_4 (aq) solution, the hydrophobic nature of tBMP kept it entrapped and solid products from the reduction of KRuO_4 were obtained inside the MOF, minimizing the material formation outside the MOF (Fig. 1c). The initial product - hydrated RuO_2 in the MOF - was further dehydrated to RuO_2 (i.e. as-synthesized RuO_2 @MOF-808-P) at ca. 140 °C in N_2 .⁴⁵ Furthermore, tunable loading amounts of the RuO_2 guest were achieved by adjusting the mass ratio between tBMP and the MOF [thermogravimetric analysis (TGA) in Supplementary Figure 4 and N_2 adsorption measurements in Supplementary Figure 5].

RuO_2 @MOF-808-P characterizations and loading control. We have confirmed the preservation of the MOF host structure throughout the synthesis of RuO_2 @MOF-808-P by its mostly unaltered powder x-ray diffraction (PXRD) patterns (Supplementary Figure 6). Pore occupation by the guest was revealed by the reduction in pore volume as shown in the pore

distributions (Supplementary Figure 5d), which were derived from the N₂ adsorption measurements. The incorporation of Ru-based guests in the MOF was confirmed with a combination of (i) energy-dispersive x-ray spectroscopy (EDS) element mappings obtained from both scanning electron microscopy (SEM) (i.e. SEM-EDS, Supplementary Figure 7) and scanning transmission electron microscopy (STEM) (i.e. STEM-EDS, Supplementary Figure 8), and (ii) X-ray photoelectron spectroscopy (XPS) (Supplementary Figure 9). The nature of the Ru-based guest was partly revealed from the XPS Ru 3p_{3/2} peak position (Supplementary Figure 10) at ca. 463.2 eV, which matches the standard Ru⁴⁺ peak.⁴⁶ X-ray absorption fine structure (XAFS) measurements (Supplementary Figure 11), using Ru foil and anhydrous RuO₂ as references, identified the dominant Ru-O vector at ca. 1.78 Å.⁴⁷ Furthermore, a dark-field STEM (DF-STEM) image (Supplementary Figure 12) shows particles (ca. 15 Å in diameter) with electron diffraction fringes. The small particle size is consistent with the PXRD results, as no X-ray diffraction peak could be found for very small guest.¹⁶ The space between two adjacent lines in the fringes is 2-2.5 Å, which matches the inter-planar spacing [$d_{(011)/(101)}$ or $d_{(200)/(020)}$] expected for tetragonal RuO₂ (space group: P4₂/mmn). Note that further reduction in adsorbed volume of N₂ can be explained by partial pore collapse and/or amorphization.^{24,48,49} This is supported by the disappearance of PXRD peaks (*i.e.* less ordered) above 40° for as-prepared RuO₂@MOF-808-P as compared with dried MOF-808-P (Supplementary Figure 13). No significant potassium (K) residual could be found by ICP-OES in the RuO₂@MOF-808-P. This is also consistent with the SEM-EDS spectrum (Supplementary Figure 7, no peak at 3.314 keV for K α) and XPS spectra (Supplementary Figure 9, no peak around 294.0 eV for K 2p).

To demonstrate the loading position control, we performed the redox reactions by adding K₂RuO₄ (aq) solution to tBMP/DE/MOF-808-P mixture with and without the temperature-controlled selective desorption (Fig. 2a). By deliberately avoiding the

205 temperature-controlled selective desorption, we obtained a significant material deposition on
206 the outer surface of the MOF (Fig. 2a, top) in the dehydrated product. Since the tBMP/DE
207 mixture on the outer surface forms droplets in contact with the KRuO_4 (aq) solution to
208 minimize the surface energy due to hydrophobic-hydrophilic repulsion, tBMP (outside the
209 MOF) can only react with KRuO_4 at the droplet-water interface forming a solid shell of
210 hydrated RuO_2 . This is consistent with the spherical shell nanostructures deposited outside
211 the MOF. The chemical composition of the spherical shell structures was verified by STEM-
212 EDS (Fig. 2b). While both Zr and Ru signals are detected from the Zr-based MOF region
213 after RuO_2 loading, only Ru signal could be collected for the spherical shell nanostructures
214 (highlighted in the yellow frame in Fig. 2b). In contrast, the dehydrated product (i.e.
215 $\text{RuO}_2@\text{MOF-808-P}$) from the reaction between KRuO_4 (aq) solution and $\text{tBMP}@\text{MOF-808-}$
216 P (with the temperature-controlled selective desorption) showed quite a clean MOF surface
217 (Fig. 2a, bottom). Furthermore, the Ru signal mapping overlaps well with that for Zr and the
218 MOF DF-STEM image (Fig. 2c). The significant outer surface deposition is therefore proved
219 to be effectively inhibited by applying both temperature-controlled selective desorption and
220 hydrophobic-hydrophilic repulsion.



221

222 **Fig. 2** Controllable RuO_2 guest formation inside (or both inside and outside) MOF-808-P. **a** RuO_2 can
 223 be formed both inside and outside the MOF, or only inside the MOF (i.e. RuO_2 @MOF-808-P) via
 224 temperature (T)-controlled selective desorption of the tBMP molecules outside the MOF. DF-STEM
 225 images to the right show spherical shell structures on the outer surface of the MOF crystals (top, for
 226 RuO_2 formed inside and outside the MOF, scale bars: 500 nm and 200 nm for left and right) vs. clean
 227 MOF crystal edges (bottom, for RuO_2 loaded mostly inside the MOF, scale bars: 500 nm and 50 nm
 228 for left and right). The controlled deposition was further verified by STEM-EDS Zr and Ru mappings
 229 for **b** RuO_2 formed inside and outside the MOF, scale bar: 200 nm, and **c** RuO_2 loaded mostly inside

the MOF, scale bar: 100 nm. The yellow frames in **b** highlight the Ru-based spherical shell structures. Raw images are provided as a Source Data file.

Weakened CO and O interactions. In heterogeneous catalysis both catalyst surface structure and molecule surface adsorption have a significant influence on the catalytic performance.^{39,50} We selected CO oxidation, which is relatively simple and well-documented for a wide range of metal-based catalysts, as a prototypical reaction to understand the significance of molecule interactions with RuO₂.^{39,51–55} Meanwhile, CO oxidation (*i.e.* elimination) is practically important for lowering automotive exhaust emissions, producing CO-free hydrogen for fuel cells and ammonia synthesis, and cleaning air, particularly at low temperatures and in humid air.^{39,52–54} At low temperatures the RuO₂ is often regarded as a poor catalyst for CO oxidation because of surface passivation.^{39,40} Below 150 °C the dominant mechanism for this reaction is the Langmuir-Hinshelwood process,^{39,40,56} in which the adsorbed CO combines with dissociated O₂ species (*i.e.* O atoms) to produce CO₂. Strong adsorption of CO and O species on RuO₂, however, usually results in the formation of densely packed CO and O domains, where the limited surface desorption and diffusion of both species cause the low catalytic activity.^{39–41} The PEGS synthesis of RuO₂@MOF-808-P allows weaker CO and O interactions with RuO₂ surface as compared to the commonly used porous silica-supported RuO₂ catalyst (RuO₂/SiO₂),^{3,17,50,57} which will be discussed below. We prepared the RuO₂/SiO₂ with a conventional impregnation method⁵⁸ and a commercially available amorphous SiO₂ with mesoporosity (Supplementary Figures 14-16). Both RuO₂/SiO₂ and RuO₂@MOF-808-P samples contained ca. 10 wt% Ru.

Ru-O interactions within the RuO₂ nanostructures were tested by CO-temperature-programmed reduction (CO-TPR), which was performed with pre-oxidized samples equilibrated in flowing CO, and then gradually heated to find the minimum temperature where the lattice Ru could be reduced (Fig. 3a). The reduction peak for RuO₂@MOF-808-P

is much sharper and at a much lower temperature ($\sim 160\text{ }^{\circ}\text{C}$) than that from $\text{RuO}_2/\text{SiO}_2$ ($\sim 240\text{ }^{\circ}\text{C}$). The result was further confirmed by in situ X-ray absorption near edge structure (XANES) spectra, which showed that $\text{RuO}_2@\text{MOF-808-P}$ was reduced more significantly than $\text{RuO}_2/\text{SiO}_2$ by 5% CO at $30\text{ }^{\circ}\text{C}$ (Supplementary Figure 17). The high reducibility of RuO_2 (i.e. weaker Ru-O bonding) within the MOF is likely the result of an electronic confinement effect, which causes bonding orbital distortion.¹⁶ Accordingly, we deduce that the interaction of O with the RuO_2 surface in $\text{RuO}_2@\text{MOF-808-P}$ was significantly weakened.

The weaker interaction of CO with the MOF-confined RuO_2 surface was revealed by temperature-dependent diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) investigations^{40,56} (Fig. 3b-d). For temperature-dependent CO desorption characterization (Fig. 3b), samples were pre-treated in 5 vol% CO with 95 vol% He gas at room temperature and then heated up to $150\text{ }^{\circ}\text{C}$ in flowing Ar. The on-top CO molecules (CO absorbed on coordinately unsaturated Ru) at the $\text{RuO}_2@\text{MOF-808-P}$ surface were lost from the surface above room temperature, and at $150\text{ }^{\circ}\text{C}$ the main peak at 2061 cm^{-1} almost disappeared (Fig. 3b). In contrast, for $\text{RuO}_2/\text{SiO}_2$ no CO desorption could be observed below $100\text{ }^{\circ}\text{C}$ and 70% of the corresponding peak intensity (2076 cm^{-1} , Fig. 3b) remains at $150\text{ }^{\circ}\text{C}$.

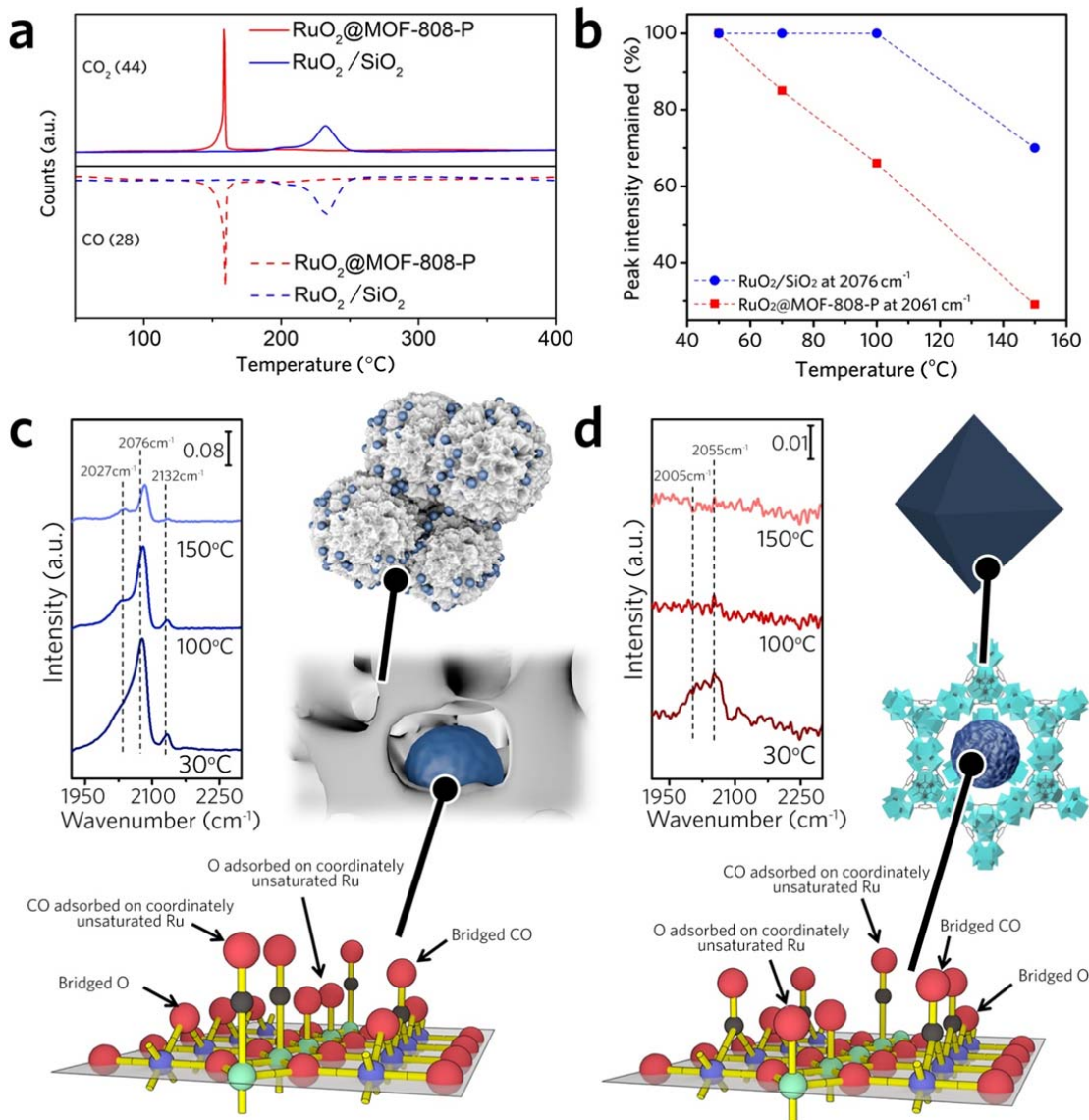


Fig. 3 CO and O interactions with RuO₂ for RuO₂/SiO₂ and RuO₂@MOF-808-P. **a** CO-TPR in flowing CO and **b** temperature-dependent DRIFTS peak intensity reduction (due to CO desorption) for samples with only surface-adsorbed CO in flowing Ar. DRIFTS results for **c** RuO₂/SiO₂ and **d** RuO₂@MOF-808-P with both surface-adsorbed CO and O in flowing Ar at various temperatures. The RuO₂ (110) surface was taken as an example to assist our interpretation of the DRIFTS results in Table 1 (O in red, C in black, and green and blue for alternating rows of Ru with different {RuO₆} octahedral orientation). Source data are provided as a Source Data file.

279 **Table 1.** DRIFTS absorption bands for RuO₂/SiO₂ and RuO₂@MOF-808-P and their indications.^{40,56}

Sample	DRIFTS band (cm ⁻¹)	CO ads. type	Indication
RuO ₂ /SiO ₂	2132	on-top	
	2076	on-top	presence of densely packed CO domains resisting CO oxidation at low temperatures
	2027	bridging	
RuO ₂ @MOF-808-P	2055	on-top	loosely packed state of CO
	2005	bridging	with even fewer adsorbed O neighbors nearby

280 Under reaction conditions close to room temperature (ca. 30 °C), DRIFTS bands also
 281 reveal the packing state of the adsorbed species, with densely packed CO adsorption domains
 282 observed on RuO₂/SiO₂ but not on RuO₂@MOF-808-P (Figs. 3c-d). In this experiment,
 283 DRIFTS spectra of both samples were collected by adsorbing CO (in 1 vol% CO, 20 vol% O₂,
 284 and 79 vol% He) at room temperature and then heating up in Ar. The DRIFTS bands are
 285 summarized in Table 1 with data interpretation supported by previous studies.^{40,56} The control
 286 experiment on pure MOF material shows no CO adsorption (no similar peak feature found in
 287 the MOF-808-P spectra, Supplementary Figure 18). The shift of on-top CO stretching
 288 frequency (2076 cm⁻¹ for RuO₂/SiO₂ versus 2055 cm⁻¹ for RuO₂@MOF-808-P) is attributed
 289 to the disappearance of the densely-packed CO domains in RuO₂@MOF-808-P.^{40,56}
 290 Meanwhile, the weakened interaction of O with RuO₂ surface, which is suggested by CO-
 291 TPR, is also supported by the change of bridging CO frequency (2027 cm⁻¹ for RuO₂/SiO₂
 292 versus 2005 cm⁻¹ for RuO₂@MOF-808-P) showing fewer O surrounding CO on the surface
 293 of the MOF-confined RuO₂.^{40,56}

294 Overall by confining the RuO₂ inside the MOF's cavity, (i) the interactions between
 295 O/CO and the catalyst (i.e. RuO₂) surface are weakened; and (ii) the formation of densely
 296 packed CO domains is inhibited. As a consequence, the adsorbed CO is more easily oxidized.

This is further reflected by the temperature-dependent DRIFTS results (Figs. 3c-d): surface CO is completely eliminated at 100 °C on the RuO₂@MOF-808-P catalysts, whereas the majority of CO molecules are still present on RuO₂/SiO₂ at 100 °C. The ability to modulate the surface adsorption of CO and O species on RuO₂ contained in the MOF's cavity have motivated us to compare the activities of CO oxidation catalyzed by RuO₂@MOF-808-P and RuO₂/SiO₂, respectively.^{50,51,57,59,60}

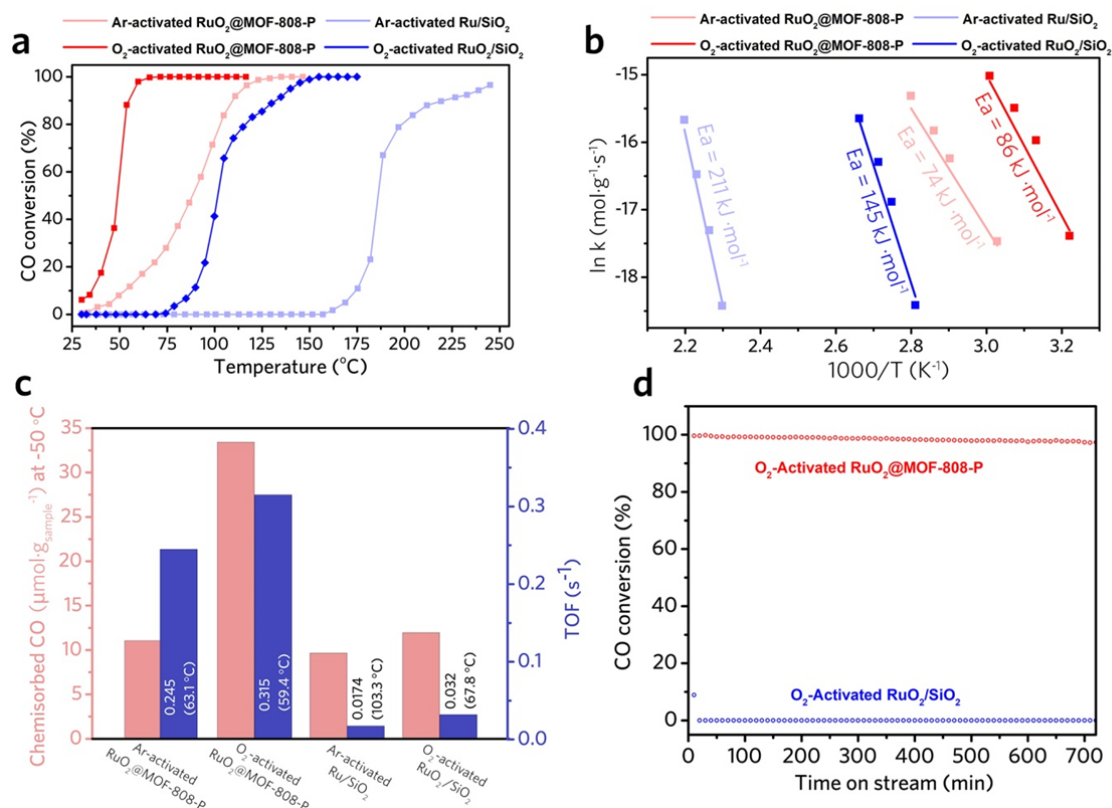


Fig. 4 CO oxidation performance over RuO₂/SiO₂ and RuO₂@MOF-808-P catalysts. **a** CO conversion profiles at weight hourly space velocity (WHSV) of 2000 L·g_{Ru}⁻¹·h⁻¹ with 15 mg catalysts; **b** Arrhenius plots and calculated apparent activation energies (E_a); **c** chemisorbed CO at -50 °C (to prevent CO₂ formation during the measurements) and calculated turn-over frequency (TOF, conversion per unit site per unit time). **d** Stability test using O₂-activated RuO₂/SiO₂ and RuO₂@MOF-808-P catalysts (2000 L·g_{Ru}⁻¹·h⁻¹, 15 mg catalysts) at 100 °C. Experimental details are given in Supplementary Section 4.2. Source data are provided as a Source Data file.

RuO₂@MOF-808-P as a low-temperature CO oxidation catalyst. Under all reaction conditions shown in Fig. 4, the RuO₂@MOF-808-P catalysts demonstrate superior performance compared with the RuO₂/SiO₂ catalysts (ca. 5% vs. no CO conversion at 30 °C; 100% at 65 °C vs. 100% at 150 °C). Meanwhile, both catalysts achieve better CO conversions at low temperature after activation in O₂ compared with activation in Ar (Fig. 4a), suggesting that oxygen-rich Ru oxide is the active surface structure for low temperature CO oxidation.⁶¹ From the CO conversion data we calculate the apparent activation energies from the MOF-confined and SiO₂-supported RuO₂ to be $E_a = 86 \text{ kJ}\cdot\text{mol}^{-1}$ and $E_a = 145 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, with the MOF-confined catalyst activation energy at the low end of the measured RuO₂ activation energies (Fig. 4b).³⁹ The remarkably higher turnover frequency (TOF) for RuO₂@MOF-808-P (Fig. 4c) than that for RuO₂/SiO₂ and those shown in Supplementary Table 1⁶² is also likely the result of the presence of loosely packed CO molecules. As controls, we have verified that MOF-808-P and tBMP@MOF-808-P are inactive for CO oxidation (Supplementary Figure 19). We can also exclude any significant contribution from the precursor (i.e. KRuO₄) to the superior catalytic performance of RuO₂@MOF-808-P by showing that the CO oxidation performance for RuO₂/SiO₂ with RuCl₃ is better than that for RuO₂/SiO₂ with KRuO₄ (Supplementary Figure 20).

The above results indicate that RuO₂@MOF-808-P is a unique low-temperature CO-oxidation catalyst. At 100 °C and 2000 L·g_{Ru}⁻¹·h⁻¹ CO flow rate, it still sustained > 97% conversion capability after 12 hrs, whereas under the same conditions RuO₂/SiO₂ deactivated completely within 20 min (Fig. 4d). This is consistent with our CO-TPR and DRIFTS results (Fig. 3). We suggest that, for the RuO₂/SiO₂ catalysts upon being exposed to the continuously fed reaction gas at low temperatures, the densely-packed surface CO and O domains form and prevent the CO-O reaction (Fig. 4c), leading to rapid deactivation at 100 °C (Fig. 4d).

By forming RuO₂@MOF-808-P using the PEGS strategy, we allow adsorbed CO to react with adsorbed O at low temperature (Fig. 3d) due to the weakened CO and O interactions with the RuO₂ surface. These modulated interactions can be attributed to the confined microenvironment provided by the MOF^{50,51,59} and/or the unique surface chemistry of RuO₂ introduced by the PEGS method. Additionally, around 30 °C we have also observed drastically different CO conversion performances (Supplementary Figures. 21 and 22); whereas the RuO₂/SiO₂ catalyst is completely deactivated after 12 min, the MOF-confined one still has > 40% conversion after 2 hrs and can be easily re-generated. This further promises normal ambient-condition based CO removal, in which pure thermal stability is no longer a major concern but potential interactions of the catalysts with water should be considered. In this context, by treating RuO₂@MOF-808-P with water vapor at 100 °C, we proved that (i) the MOF structure is mostly preserved (Supplementary Figure 23) and (ii) the RuO₂@MOF-808-P retains its high activity (Supplementary Figure 24), which has been a challenge for recent MOF-based catalyst development.⁶³

Discussion

In summary, we use a preparation of RuO₂@MOF-808-P as a tutorial to introduce the PEGS strategy, which enables the formation of guests confined in metastable hosts by rational selection of the precursors and conditions for their synthesis. The successful synthesis of RuO₂@MOF-808-P results in modulated CO/O adsorption behavior and a remarkable improvement in the CO oxidation performance on the RuO₂ surface at low temperatures. The PEGS method can be extended to other guests and nanoporous hosts with reasonable stability under desired synthesis conditions (Supplementary Figure 25).^{24,64} In theory, the PEGS approach is applicable to metals, oxides, hydroxides and sulfides⁶⁵ as long as their relevant Pourbaix diagrams indicate the feasibility of their formation. So far, we have attempted oxides (i.e. RuO₂ and MnO_x) with different MOFs (MOF-808-P and DUT-67⁶⁶) and a zeolite

Y²⁰ (Supplementary Figure 25), and Pd metal particles with MOF-808-P (Supplementary Figures 26-28). Furthermore, benefiting from the recent development of the materials genome approach and the continuous expansion of available databases of Pourbaix diagrams or related phase diagrams (e.g. Materials Project⁶⁷⁻⁷⁰), it may even be possible to design guests with more complicated chemistries (e.g. nitrides, phosphides and multi-element compounds). Additionally, considering parameters determining the reactivity in other solvents, diagrams similar to Pourbaix diagrams may be constructed for water-free synthesis. The functions of such guests are not limited solely to catalysis, but could be used to produce a wide variety of optoelectronic materials.^{2,18} We believe that this rational synthesis approach to guest functionality in MOF hosts will become a general tool for the systematic synthesis of homologous series of guests confined in porous hosts, as well as a route for combinatorial discovery of materials towards novel practical significance.

Methods

Sample Preparation. Detailed experimental methods can be found in the Supplementary Information. The considerations to plan a guest synthesis are mentioned in the Supplementary Information 1 and 2.1. To prepare the RuO₂@MOF-808-P, briefly, MOF-808-P was produced first using a method based on a previously reported synthesis (Supplementary Section 2.3).³⁶ The dried MOF-808-P was loaded with tBMP-in-DE solution (50 mg tBMP with 1 ml DE, detailed in Supplementary Section 2.4). The tBMP-to-MOF-808-P mass ratio in the mixture was adjusted to control the final loading of RuO₂ (Supplementary Figure 5a). The as-prepared tBMP/DE@MOF-808-P powder was then heated at 120 ± 5 °C under N₂ flow for ca. 1 hr (i.e. temperature-controlled selective desorption) to remove the tBMP outside the MOF and DE (Supplementary Section 2.4, Supplementary Figure 3). The treated material was immersed in an excess amount of K₂RuO₄ aqueous solution (20 mM) for ca. 4 hrs to form hydrous RuO₂@MOF-808-P. It was finally collected by filtration and dehydrated at ca.

140 °C to give as-synthesized RuO₂@MOF-808-P (Supplementary Section 2.5). Methods for RuO₂/SiO₂ preparation and characterizations are given in Supplementary Section 3.1.

Materials characterization. Methods for RuO₂@MOF-808-P characterizations are given in Supplementary Section 2.6.

Surface adsorption and CO oxidation investigations. Methods for surface adsorption and CO oxidation investigations are given in Supplementary Section 4.1.

Data Availability

The authors declare that all data supporting the findings of this study are included in the paper and its supplementary information files, and are available on request from the corresponding authors. The raw images and/or source data underlying Figs. 2-4 and Supplementary Figures. 3-25, 27 and 28 are provided as a Source Data fileset, which is also available in figshare (doi: 10.6084/m9.figshare.7588250).

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Author contributions

The manuscript is written through contributions of all authors. All authors have given approval to the final version of the manuscript. T.W., who is supervised by S.K.S. and co-advised by A.K.C. and R.V.K., initiated the project and developed the PEGS. X.B., Q.F., S.K.S., A.K.C., T.W. and L.G. conceived the idea about using RuO₂@MOF-808-P for CO oxidation. T.W. prepared RuO₂@MOF-808-P. J.H., S.J.A.H., J.T.G., W.L. S.G. and T.W. characterized RuO₂@MOF-808-P guided by S.K.S., A.K.C., R.V.K. and M.-M.T.. L.G. and J.D. characterized CO adsorption and CO oxidation supervised by X.B. and Q.F.. T.W., L.G. and J.H. prepared the initial manuscript instructed by S.K.S., X.B., Q.F., A.K.C., R.V.K. and M.-M.T. with input from all the authors.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to S.K.S. and Q.F..

Competing financial interests

The authors declare the following competing financial interest(s): A relevant patent is filed by T.W., S.K.S., Q.F. and L.G. (GB1813334.8). The other authors declare no competing financial interests.