Rational approach to guest confinement inside MOF cavities for low-temperature catalysis

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Geometric or electronic confinement of guests inside nanoporous hosts promises to deliver unusual catalytic or opto-electronic functionality from existing materials but is challenging to obtain particularly using metastable hosts, such as metal-organic frameworks (MOFs). Reagents (e.g. precursor) may be too large for impregnation and synthesis conditions may also destroy the hosts. Here we use thermodynamic Pourbaix diagrams (favorable redox and pH conditions) to describe a general method for metal-compound guest synthesis by rationally selecting reaction agents and conditions. Specifically we demonstrate a MOF-confined RuO₂ catalyst (RuO₂@MOF-808-P) with exceptionally high catalytic CO oxidation below 150 °C as compared to the conventionally made SiO₂-supported RuO₂ (RuO₂/SiO₂). This can be caused by weaker interactions between CO/O and the MOF-encapsulated RuO₂ surface thus avoiding adsorption-induced catalytic surface passivation. We further describe applications of the Pourbaix-enabled guest synthesis (PEGS) strategy with tutorial examples for the general synthesis of arbitrary guests (e.g. metals, oxides, hydroxides, sulfides).
loading guests (e.g., molecules, clusters or particles) inside the pre-existing pores of nanoporous hosts (guest@-nanoporous-host) is one of the key post-synthesis modification strategies for porous materials. It can yield highly active and stable heterogeneous catalysts as well as robust photo/elec-
tro-luminescence materials and supramolecular cages (i.e., host–guest chemistry and/or inclusion chemistry). Besides metal particles/clusters, however, such synthesis is still challenging or impossible for other types of guest particles/clusters (e.g., oxides, hydroxides, sulfides, nitriles, phosphides) inside the host’s cavity/channel. Many hosts have very small aperture (a.k.a. window) opening sizes (typically <2 nm), and hence direct impregnation of guest compounds with much larger sizes is no longer feasible. Guests, therefore, have to be assembled locally within the cavity/channel (i.e., ship-in-a-bottle assembly). The general ‘ship-in-a-bottle’ approach is to load smaller precursors (e.g., salts and organometallics) into pre-formed porous host materials via solution-based, gas-phase or mechanical-mixing impregnation, followed by either thermal/photochemical decomposition or redox reaction (with either strong redox reagents, e.g., hydrazine and NaBH₄, or high-temperature treatment in reducing atmosphere, e.g., H₂). These methods which are useful for bulk or nanostructure synthesis (i.e., unconfined systems) often fail to work properly in nanoporous hosts. The major dilemmas are that (i) many of the reactants are still too large to be impregnated and (ii) the conditions required to form a target guest may damage or destroy the host structure. Nonetheless, the ship-in-a-bottle strategy has been recently recognized as a promising way to post-synthetically functionalize porous metal–organic frameworks (MOFs) which are host matrices assembled with metal centers and organic ligands with extremely diverse chemistries, topologies and pore architectures. By immobilizing the guests inside MOFs, guest aggregation/fusion can be effectively prevented. Meanwhile, MOF hosts have been found to influence the properties of the guests, e.g., modulation of electron–hole recombination rates for quantum dots. Hence, there is a demand to carry out ship-in-a-bottle synthesis with sufficiently small reaction reagents under mild conditions, as many of these metastable MOFs suffer from poor chemical and thermal stability. A rational route for incorporation of guest compounds into an arbitrary nanoporous host should enable the investigation of multiple host–guest systems with surprising functionalities.

We realize that the synthetic conditions of guests can be pre-determinable based on pH/potential-dependent equilibrium solid/solution maps (well known by materials scientists as Pourbaix diagrams, e.g., Fig. 1a), which have been extensively investigated and used for depicting relevant thermodynamics during a corrosion process (normally solid → solution). Instead of studying solid → solution reactions, we use the Pourbaix diagrams to select precursor solutions and synthetic conditions (i.e., redox potential and/or pH) to solidify the desired guests (i.e., solution → solid processes) within the pores of the hosts. We term this strategy Pourbaix enabled guest synthesis (PEGS) (Fig. 1a, Supplementary Section 1). Briefly, by checking the Pourbaix diagrams we can find the difference in the redox potential (ΔE) and/or pH between a soluble guest precursor and a desired guest. We can then shortlist the hosts and reagents (e.g., precursors) that meet the guest formation requirements and select the most appropriate candidates perhaps with other properties (i.e., desired boiling temperature and hydrophobicity) to manage the ship-in-a-bottle synthesis.

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

The ability to synthesize a large variety of catalytic and optoelectronic materials with an even greater variety of available and synthesizable MOF materials is a combinatorial treasure trove of potential discoveries. We demonstrate the synthesis of RuO₂ inside MOF-808-P. We used potassium perruthenate (K₂RuO₄) 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)
Diethyl ether (DE) is used as a solvent for tBMP. The pH range is known to provide a certain range of potentials where a certain phase is thermodynamically stable, with the potential needed to transform one phase to another. We have seen that at a pH of ca. 8.5 (20 mM aqueous potassium perruthenate (KRuO$_4$)), one needs minimum reduction potential ($\Delta E_{\text{red}}$) 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. Therefore, a small reducing reagent which matches this $\Delta E_{\text{red}}$ 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. We expect that if it also provides $\sim$0.3 V of oxidation potential, it may be sufficient to reduce RuO$_4^-$ to RuO$_2$·2H$_2$O within a controlled pH range of 5–10.

![Pourbaix diagram for Ru-H$_2$O system](Fig_1a.png)

**Fig. 1** Pourbaix enabled guest synthesis (PEGS) strategy for RuO$_2$ incorporation into MOF-808-P. **a** Pourbaix (redox potential-pH) diagram for Ru-H$_2$O system (with a pH range of 5-10; concentration of Ru-based solution $\sim$ 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 (RuO$_4^-$), to solid Ru-based guest (i.e., RuO$_2$·2H$_2$O) at a pH of ca. 8.5 (20 mM aqueous potassium perruthenate (KRuO$_4$)), one needs minimum reduction potential ($\Delta E_{\text{red}}$) 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** Symbols for the scheme in (a), which illustrates RuO$_2$ synthesis inside the cavity of pre-formed MOF-808-P by using the hydrophobic reducing lipid tBMP. For clarity (i) the schematics of MOF-808-P is simplified as standard MOF-808$^{36}$ and (ii) hydrogen atoms and carbon atoms for formates (HCOO$^-$) are omitted in the metal-organic framework (MOF) cage.
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 3P3/2 peak position (Supplementary Figure 10) at ca. 463.2 eV, which matches the standard Ru4+ peak46. X-ray absorption fine structure measurements (Supplementary Figure 11), using Ru foil and anhydrous RuO2 as references, identified the dominant Ru-O vector at ca. 1.78 Å47. 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 guest16. 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/mnm). Note that further reduction in adsorbed volume of N2 can be explained by partial pore collapse and/or amorphization24,48,49. 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 inductively coupled plasma-optical emission spectrometry (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 Kα) 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 KRuO4 (aq) solution to tBMP/DE/MOF-808-P mixture with and without the temperature-controlled selective desorption (Fig. 2a). By deliberately avoiding the temperature-controlled selective desorption, we obtained a significant material deposition on the outer surface of the MOF (Fig. 2a, top) in the dehydrated product. Since the tBMP/DE mixture on the outer surface forms droplets in contact with the KRuO4 (aq) solution to minimize the surface energy due to hydrophobic–hydrophilic repulsion, tBMP (outside the MOF) can only react with KRuO4 at the droplet-water interface forming a RuO2·2H2O formation

\[ \text{tBMP with KRuO}_4(\text{aq}) \rightarrow \text{RuO}_2@\text{MOF} \]

Fig. 2 Controllable RuO2 guest formation inside (or both inside and outside) MOF-808-P. a RuO2 can be formed both inside and outside the metal–organic framework (MOF), or only inside the MOF (i.e., RuO2@MOF-808-P) via temperature (T)-controlled selective desorption of the 2-tert-butyl-4−methylphenol (tBMP) molecules outside the MOF. Dark-field scanning transmission electron microscopy (DF-STEM) images to the right show spherical shell structures on the outer surface of the MOF crystals (top, for RuO2 formed inside and outside the MOF, scale bars: 500 nm and 200 nm for left and right) vs. clean MOF crystal edges (bottom, for RuO2 loaded mostly inside the MOF, scale bars: 500 nm and 50 nm for left and right). The controlled deposition was further verified by STEM-energy-dispersive X-ray spectroscopy (EDS) Zr and Ru mappings for b RuO2 formed inside and outside the MOF, scale bar: 200 nm, and c RuO2 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.
solid shell of hydrated RuO₂. This is consistent with the spherical shell nanostructures deposited outside the MOF. The chemical composition of the spherical shell structures was verified by STEM-EDS (Fig. 2b). While both Zr and Ru signals are detected from the Zr-based MOF region after RuO₂ loading, only Ru signal could be collected for the spherical shell nanostructures (highlighted in the yellow frame in Fig. 2b). In contrast, the dehydrated product (i.e., RuO₄@MOF-808-P) from the reaction between K RuO₄ (aq) solution and tBMP@MOF-808-P (with the temperature-controlled selective desorption) showed quite a clean MOF surface (Fig. 2a, bottom). Furthermore, the Ru signal mapping overlaps well with that for Zr and the MOF DF-STEM image (Fig. 2c). The significant outer surface deposition is therefore proved to be effectively inhibited by applying both temperature-controlled selective desorption and hydrophobic–hydrophilic repulsion.

**Weakened CO and O interactions.** In heterogeneous catalysis both catalyst surface structure and molecule surface adsorption have a significant influence on the catalytic performance. 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 RuO₄. 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. At low temperatures, the RuO₂ is often regarded as a poor catalyst for CO oxidation because of surface passivation. Below 150 °C, the dominant mechanism for this reaction is the Langmuir–Hinshelwood process, 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. 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 method, 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 (~160 °C) than that from RuO₂/SiO₂ (~240 °C). The result was further confirmed by in situ X-ray absorption near edge structure (XANES) spectra, which showed that RuO₂@MOF-808-P was reduced more significantly than RuO₂/SiO₂ by 5% CO at 30 °C (Supplementary Figure 17). The high reducibility of RuO₂ (i.e., weaker Ru-O bonding) within the MOF is likely the result of an electronic confinement effect, which causes bonding orbital distortion. Accordingly, we deduce that the interaction of O with the RuO₂ surface in RuO₂@MOF-808-P was significantly weakened.

The weaker interaction of CO with the MOF-confined RuO₂ surface was revealed by temperature-dependent diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) investigations (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 °C in flowing Ar. The on-top CO molecules (CO adsorbed on coordinately unsaturated Ru) at the RuO₂@MOF-808-P surface were lost from the surface above room temperature, and at 150 °C the main peak at 2061 cm⁻¹ almost disappeared (Fig. 3b). In contrast, for RuO₂/SiO₂ no CO desorption could be observed below 100 °C and 70% of the corresponding peak intensity (2076 cm⁻¹, Fig. 3b) remains at 150 °C.

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

Overall by confining the RuO₂ inside the MOF cavity (i) the interactions between O/CO and the catalyst (i.e., RuO₂) surface are weakened; and (ii) the formation of densely 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 (Fig. 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 cavity has motivated us to compare the activities of CO oxidation catalyzed by RuO₂@MOF-808-P and RuO₂/SiO₂, respectively. 

**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. From the CO conversion data we calculate the apparent activation energies from the MOF-confined and SiO₂-supported RuO₂ to be $E_a = 86$ kJ mol⁻¹ and $E_a = 145$ kJ mol⁻¹, respectively, with the MOF-confined catalyst activation energy at the low end of the measured RuO₂ activation energies (Fig. 4b). The remarkably higher turnover frequency (TOF) for RuO₂@MOF-808-P (Fig. 4c) than that for RuO₂/SiO₂ and those shown in Supplementary Table 1 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 RuO$_2$@MOF-808-P is a unique low-temperature CO oxidation catalyst. At 100 °C and 2000 L g$_{\text{Ru}}^{-1}$ h$^{-1}$ CO flow rate, it still sustained >97% conversion capability after 12 h, whereas under the same conditions RuO$_2$/SiO$_2$ deactivated completely within 20 min (Fig. 4d). This is consistent with our CO-TPR and DRIFTS results (Fig. 3). We suggest that, for the RuO$_2$/SiO$_2$ 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 RuO$_2$@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 RuO$_2$ surface. These modulated interactions can be attributed to the confined microenvironment provided by the MOF and/or the unique surface chemistry of RuO$_2$ 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 RuO$_2$/SiO$_2$ catalyst is completely deactivated after 12 min, the MOF-confined one still has >40% conversion after 2 h 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 RuO$_2$@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 RuO$_2$@MOF-808-P retains its high activity (Supplementary Figure 24), which has been a challenge for recent MOF-based catalyst development.$^{63}$

**Fig. 3** CO and O interactions with RuO$_2$ for RuO$_2$/SiO$_2$ and RuO$_2$@MOF-808-P. **a** CO-temperature-programmed reduction (CO-TPR) in flowing CO and **b** temperature-dependent diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) peak intensity reduction (due to CO desorption) for samples with only surface-adsorbed CO in flowing Ar. DRIFTS results for (c) RuO$_2$/SiO$_2$ and (d) RuO$_2$@MOF-808-P with both surface-adsorbed CO and O in flowing Ar at various temperatures. The RuO$_2$ (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 {RuO$_6$} octahedral orientation). Source data are provided as a Source Data file.
In summary, we use a preparation of RuO$_2$@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 RuO$_2$@MOF-808-P results in modulated CO/O adsorption behavior and a remarkable improvement in the CO oxidation performance on the RuO$_2$ 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)\textsuperscript{24,64}. In theory, the PEGS approach is applicable to metals, oxides, hydroxides and sulfides\textsuperscript{65} as long as their relevant Pourbaix diagrams indicate the feasibility of their formation. So far, we have attempted oxides (i.e., RuO$_2$ and MnO$_x$) with different MOFs (MOF-808-P and DUT-67)\textsuperscript{66} and a zeolite Y\textsuperscript{20} (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 Project\textsuperscript{67–70}), 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\textsuperscript{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.

### Table 1 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) absorption bands for RuO$_2$/SiO$_2$ and RuO$_2$@MOF-808-P and their indications\textsuperscript{40,56}

| Sample             | DRIFTS band (cm$^{-1}$) | CO ads. type | Indication                                           |
|--------------------|-------------------------|--------------|------------------------------------------------------|
| RuO$_2$/SiO$_2$    | 2132                    | On-top       | Presence of densely packed CO domains resisting CO oxidation at low temperatures |
|                    | 2076                    | On-top       |                                                     |
|                    | 2027                    | Bridging     |                                                     |
| RuO$_2$@MOF-808-P  | 2055                    | On-top       | Loosely packed state of CO                           |
|                    | 2005                    | Bridging     | With even fewer adsorbed O neighbors nearby          |

**Fig. 4** CO oxidation performance over RuO$_2$/SiO$_2$ and RuO$_2$@MOF-808-P catalysts. **a** CO conversion profiles at weight hourly space velocity (WHSV) of 2000 L g$\text{Ru}^{-1}$ h$^{-1}$ with 15 mg catalysts. **b** Arrhenius plots and calculated apparent activation energies ($E_a$). **c** Chemisorbed CO at $-50$ °C (to prevent CO$_2$ formation during the measurements) and calculated turnover frequency (TOF, conversion per unit site per unit time). **d** Stability test using O$_2$-activated RuO$_2$/SiO$_2$ and RuO$_2$@MOF-808-P catalysts (2000 L g$\text{Ru}^{-1}$ 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.
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).20 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 h (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 KRuO2 aqueous solution (20 mM) for ca. 4 h 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.

Material characterization. The methods for RuO2@MOF-808-P characterizations are given in Supplementary Section 2.6.

Surface adsorption and CO oxidation investigations. The 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 file, which is also available in figshare (https://doi.org/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.

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