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Coupling Molecular and Nanoparticle Catalysts on Single Metal-Organic Framework Microcrystals for the Tandem Reaction of H₂O₂ Generation and Selective Alkene Oxidation

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KEYWORDS: Tandem reaction, Metal-organic framework, in situ H₂O₂ generation, alkene oxidation, UiO-66

ABSTRACT: A molecular catalyst, (sal)Mo^{VI}, and a heterogeneous catalyst, either Pd or Au nanoparticles (NPs), were integrated into one UiO-66 MOF microcrystal. The resulting dually functionalized catalysts, **Pd@UiO-66-(sal)Mo** and **Au/UiO-66-(sal)Mo**, have been utilized for a one-pot tandem reaction of H_2O_2 generation and selective liquid-phase alkene oxidation. The NPs serve as catalysts for the production of H_2O_2 from H_2 and O_2 gases, while the (sal)Mo moieties function as the oxidation catalyst. When the metal NPs are fully encapsulated within the MOF microcrystals, the alkene hydrogenation side reaction is largely suppressed, with a 6-fold decrease in the hydrogenation/oxidation product ratio for 5-bromo-1-cyclooctene favoring the epoxide as the major product. For **Au/UiO-66-(sal)Mo**, where the two catalysts are in close proximity on the MOF microcrystal, the enhancement in oxidation productivity is increased by 10 times in comparison to the [**Au/UiO-66-NH**₂ + **UiO-66-sal(Mo**)] physical mixture of the two singly functionalized MOFs.

As key chemical intermediates for the syntheses of many fine chemicals and pharmaceuticals, epoxides are traditionally obtained from the selective oxidation of alkenes in the presence of peracids and organic peroxide.¹ Given that these oxidants are usually obtained from the reaction of an organic precursor with hydrogen peroxide (H₂O₂), there have been major efforts to develop catalysts that can directly utilize H₂O₂ for alkene epoxidation. A major commercial success in this direction is the use of the titanium silicalite-1 (TS-1) catalyst for the oxidation of propylene by H₂O₂ as industrially practiced by Dow and BASF in the production of propylene oxide.² While H₂O₂ is highly attractive as a primary oxidant given its high percentage of active oxygen (47 wt %) and the formation of water as an environmentally friendly byproduct,³ its storage and transportation can pose additional safety concerns and operational costs. In addition, an excess of H₂O₂ is frequently required in other organic oxidations, attributable to its intrinsic instability. (H₂O₂ can readily decomposes into water and O₂ at moderate temperatures, in the presence of catalysts/impurities, or with small changes in reaction pH.⁴)

To overcome the problems associated with the efficient use handling H_2O_2 in alkene oxidation, a one-pot tandem reaction that directly generates H_2O_2 and employs it *in situ* (Scheme 1, Eq 1)² has been proposed by researchers. Two catalysts can be used in such a reaction, one for producing H_2O_2 and the other for the subsequent oxidation step. Given that H_2O_2 can safely be generated from H_2 and O_2 gases in the presence of Pd or Au nanoparticles (NPs) (see Supporting Information (SI), Section S1 for further safety discussion),⁵⁻⁷ these NP catalysts are highly attractive candidates for the H_2O_2 -generating step. As an example, Au/TS-1 catalysts have been extensively examined as a tandem catalyst for gas-phase propylene epoxidation,^{8,9,10} where Au NPs serves as the primary catalyst for H_2O_2 generation and Au-Ti sites are the main active species for oxidation.¹¹ Unfortunately, these noble-metal NPs are also known to be active catalysts for alkene hydrogenation (Scheme 1, Eq 2),¹²⁻¹³ and it is this secondary catalytic pathway that can significantly decrease the overall selectivity towards the desired oxidation of the carbon-containing substrate.¹⁴⁺¹⁷ Thus, we set out to search for a strategy that can suppress the alkene hydrogenation pathway in NP-catalyzed H_2O_2 -generation. From a synthetic viewpoint, suppressing this pathway would be highly attractive in increasing selectivity for the valuable epoxide products.

Scheme 1. A schematic of the reaction manifolds for the tandem *in situ* generation of H_2O_2 and alkene oxidation^{*a*}



^{*a*}We note in passing that the NPs used in this tandem scheme can also catalyze other side reactions such as combustion of hydrogen, hydrogenation of H_2O_2 , and decomposition of H_2O_2 (left side of the scheme), all of which can reduce the selectivity toward H_2O_2 generation.⁶

Although current efforts to couple H₂O₂ generation and alkene oxidations have primarily been focused on gas-phase reactions via flow processes with simple alkenes such as propylene, ^{2,18-20} we are also interested in the possibility of extending this concept to liquid-phase reactions¹⁴ that can encompass a wider scope of alkene substrates. However, carrying out such reactions in solution, particularly for batch processes, requires that we address two challenging criteria. First, the two different types of catalysts need to be deployed within a close proximity to decrease the degree of diffusion and decomposition of H₂O₂. Second, an additional selectivity screen would be necessary to prevent exposing the alkene substrate to both catalysts, which would cause hydrogenation side reaction in addition to the desirable tandem reaction combination. Using microcrystals of metal-organic frameworks (MOFs) as a platform to host and couple two different catalysts could be an ideal strategy to fulfill these criteria given recent reports on the controlled positioning of various catalysts into MOF crystals²¹ and the demonstration of molecular-size selectivity in MOFs.²⁶⁻²⁸

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Herein, we report a dually functionalized catalyst system based on MOFs to demonstrate the tandem H_2O_2 generation/selective alkene-oxidation concept (Figure 1). The metal NPs are encapsulated within one microcrystal of UiO-66-NH₂ MOF whose surfaces are modified with a (sal)Mo^{VI} (sal = salicylaldimine) molecular epoxidation catalyst. The MOF aperture is large enough to allow the small H_2 and O_2 gases to come into contact with the encapsulated NP catalysts to generate H_2O_2 which is then released into the reaction media; at the same time, this "gated window"²⁹ can prevent the larger alkene substrate from coming into contact with the NPs to undergo the undesirable hydrogenation. In such a scenario, the molecular alkene oxidation catalyst moieties are most effective when positioned at the surface of the MOF microcrystals where they can mediate the oxidation of the alkene substrate using the *in-situ* generated H_2O_2 . In such manners, the MOF crystal acts as a molecular-size "gatekeeper", allowing the dual catalyst functionalities to accomplish the desired tandem H_2O_2 -generation/cyclooctene-epoxidation reaction with minimum alkene hydrogenation. In addition, such a tandem catalyst combination in one microcrystal will produce the desired oxidation products at a higher productivity than the corresponding physical mixture of two singly modified catalysts (i.e., a MOF-encapsulated NP catalyst and a MOF-supported (sal)Mo catalyst) due to the close proximity and lesser degree of diffusion needed.



Figure 1. A schematic illustration of a dually functionalized MOF catalyst for the tandem reaction of H_2O_2 generation and selective alkene oxidation. The Pd NPs are encapsulated inside the MOF microcrystal, whose surface are functionalized with sal(Mo) moieties.

Scheme 2. The preparation of singly and dually functionalized MOF catalysts



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Synthesis of MOF-based catalysts. As the MOF support of choice, we selected the UiO-66 series, which has the proper aperture size and excellent stability in protic media;³⁰⁻³² can be used to encapsulate noble-metal NPs;^{22,33-36} and can be functionalized with molecular catalysts.³⁷⁴⁰ Encapsulation of Pd and Au NPs inside UiO-66 crystals still allows easy access for H₂ and O₂ through the ~6 Å aperture⁴¹ of the MOF and the subsequent release of H₂O₂ while selectively excluding larger alkene substrates such as *cis*-cyclooctene. For the molecular alkene oxidation catalyst, we chose (sal)Mo, a moiety that has been tethered onto UiO-66-NH₂ and has shown activity towards the epoxidation of *cis*-cyclooctene in the presence of H₂O₂,³⁸ albeit at elevated temperature.

As shown in Scheme 2, Pd@UiO-66-NH2, in which Pd NPs are encapsulated inside MOF crystals are synthesized via a de novo method modified from a previous report⁴² (see SI, Section S2 for the synthesis procedure and Section S3 for the characterization data). This material is then post-synthetically functionalized with salicylaldehyde and $MoO(O_2)_2 \cdot 2$ DMF to create the dually functionalized Pd@UiO-66-sal(Mo) MOF in two steps,³⁸ as confirmed by ICP-OES (Table 1) and FT-IR (SI, Figures S6 and S7). The PXRD patterns of the modified MOFs indicated the material remained crystalline (SI, Figures S3 and S4). TEM analysis confirmed the presence of encapsulated Pd NPs (6.1 ± 0.9 nm) throughout the MOF microcrystals (550 nm) (Figure 2). The decrease in the BET surface areas³⁸⁻⁴⁰ compared to that of Pd@UiO-66-NH₂ was consistent with the sal(Mo) modification, which added mass and partially blocked the pores of the surface layers of the MOF crystals (SI, Table S1, entries 2 and 8). To elucidate the effects of the individual catalyst components, we also synthesized two other materials (Scheme 2): 1) Pd/UiO-66-NH₂, where the NPs were formed via a wetness-impregnation method⁴³ so that Pd NPs are distributed both inside the MOF crystals and on their exterior surfaces; 2) Pd-PVP/UiO-66-NH₂, where the PVP-capped Pd NPs44 were first synthesized in colloidal solution and then attached to only the exterior surface of the MOF crystals.

While we initially set out to examine compositions that comprise either Pd or Au NPs, which are known to have very different activities for H_2O_2 generation, preliminary experiments suggested that synthesizing Au@UiO-66-NH₂ material via a *de novo* method is difficult to achieve. As such, we adapted a double-solvent/H₂-reduction method³⁵ to synthesize Au/UiO-66-NH₂ as an alternative, where the Au NPs are distributed mainly inside the MOF crystals, albeit with a small amount on the exterior surfaces. All three classes of NPcontaining MOFs maintained good porosities (SI, Table S1, entries 4-6) and showed persistence of crystallinities (SI, Figure S3) as shown by BET surface area measurements and PXRD analysis, respectively.

To evaluate the effect of the relative positioning of the two catalyst components, the (sal)Mo derivatives **Pd/UiO-66-sal(Mo)**, **Au/UiO-66-sal(Mo)**, **Pd-PVP/UiO-66-sal(Mo)**, and **UiO-66-sal(Mo)** were synthesized from the corresponding amino-functionalized derivatives. Using the previously discussed two-step post-synthesis modification (Scheme 2),³⁸ all four materials can be obtained with comparable Mo loadings to that of **Pd@UiO-66-sal(Mo)** (Table 1), as indicted by ICP-OES analysis. Transmission FT-IR analysis (SI, Figures S6 and S7) again confirmed the incorporation of the (sal)Mo functionalities. The PXRD patterns of these materials (SI, Figures S3 and S4) were similar to those of the parent MOFs,

indicating the preservation of crystallinity and long-range ordering. TEM images confirmed the presence of the NPs, on/in the MOF crystals (Figure 2). As in the case of **Pd@UiO-66sal(Mo)**, the BET surface areas of these four (sal)Mo derivatives decreased proportionately from those of the parent MOFs (SI, Table S1).





Figure 2. TEM images of the MOF materials before catalysis. To guide the readers' eyes, the position of some of the NPs on the MOF microcrystals for Pd-PVP/UiO-66-sal(Mo) and Pd/UiO-66-sal(Mo) have been indicated with white arrows. Comparing the TEM images of these samples to that of Pd@UiO-66-sal(Mo) suggests two different types of NP distributions. The NPs in the Pd@UiO-66-sal(Mo) sample are positioned throughout the middle part of the crystals because most of them are fully encapsulated inside the MOF crystals.

Activities of NP-containing catalysts for H₂O₂ production. All catalyst samples and controls were separately tested for their activities towards H₂O₂ production from H₂ and O₂ gases (for the NP-containing catalysts) and alkene oxidation (for the (sal)Mo-containing catalysts). The catalytic generation of H_2O_2 was evaluated using a batch reactor in a 7/3 v/v methanol/water solvent mixture that was reported to be safe and optimal in productivity for this reaction (see SI, Section S1 for further safety discussion),⁴⁵⁻⁴⁷ presumably due to a combination of the good solubilities of H₂ and O₂ gases⁶ as well as the protic nature of the media.⁴⁸ As expected, the control UiO-66-NH₂ and UiO-66-sal(Mo) did not produce any H₂O₂ (Table 2, entries 2-3). In contrast, all Pd-containing catalysts were highly active, producing > 200 mol $H_2O_2/h/kg_{NPs}$ at room temperature (Table 2, entries 4-6), (see SI, Section S5 for additional discussion on the effectiveness of the catalysts and their H₂ selectivity). Au/UiO-66-NH₂ also produced H₂O₂, albeit at a slower rate than the Pd-containing materials (Table 2, cf entries 7 and 5), consistent with literature reports.45-47

Table 1. The NP Sizes, NP Loadings, and Mo Loadings for UiO-66-NH₂ Derivatives

| Catalyst | NP size (nm) | NP loading $(wt\%)^a$ | Mo loading (wt%) |
|-------------------------------|-----------------|-----------------------|---------------------|
| Pd@UiO-66-NH ₂ | - | 3.2 | - |
| Pd/UiO-66-NH ₂ | - | 6.2 | - |
| Au/UiO-66-NH ₂ | - 6.6 | | - |
| Pd-PVP/UiO-66-NH ₂ | - | 2.5-3.3 ^b | - |
| Pd@UiO-66-sal(Mo) | 6.1 ± 0.9 | 1.7 | 16 |
| Pd/UiO-66-sal(Mo) | 4.9 ± 1.0 | 2.4 | 17 |
| Au/UiO-66-sal(Mo) | 9.1 ± 2.8 | 4.3 | 16 |
| Pd-PVP/UiO-66-sal(Mo) | 3.6 ± 1.1 | 1.4 | 17 |
| UiO-66-sal(Mo) | - | - | 16-18 ^b |

^{*a*}After the modification of amine ligand and the incorporation of Mo complex, the NP loadings in wt % decreased due to an increase in the total mass of catalyst (see SI, Section S7 for the supporting calculation). ^{*b*}The range of loading is from experimental variations.

 Table 2. The Catalytic Activity of MOF-Based Catalysts in

 H2O2 Generation

| $H_{0} + O_{0}$ | Catalyst | H ₂ O ₂ |
|-----------------|--|-------------------------------|
| 112 . 02 | CH ₃ OH/H ₂ O, rt, 1 h | |
| | | |

| Entry | Catalyst | NPs (mg) | $H_2O_2^a$ (mM) | H ₂ O ₂ productivity ^a (mol/h/kg _{NPs}) |
|-------|-------------------------------------|-------------------------|-----------------|--|
| 1 | - | - | 0 | 0 |
| 2 | UiO-66-NH ₂ ^b | - | 0 | 0 |
| 3 | UiO-66-sal(Mo) ^c | - | 0 | 0 |
| 4 | Pd@UiO-66-NH ₂ | 0.5 | 7.0 ± 0.8 | 273 ± 31 |
| 5 | Pd/UiO-66-NH ₂ | 0.5 | 6.3 ± 0.3 | 248 ± 12 |
| 6 | Pd-PVP/UiO-66-NH ₂ | 0.5 | 6.6 ± 0.7 | 259 ± 28 |
| 7 | Au/UiO-66-NH ₂ | 2.6 ^{<i>d</i>} | 0.3 ± 0.3 | 12 ± 10 |
| 8 | Pd@UiO-66-NH2 ^e | 0.5 | 1.9 ± 0.1 | 12 ± 0.5 |

Reaction conditions: $5\% H_2/CO_2$ (250 psig), $25\% O_2/CO_2$ (100 psig), CH₃OH (14 mL), and H₂O (6 mL). ^{*a*}The amount of H₂O₂ generated was determined by colorimetric titration with a 5 mM Ti(SO₄)₂ indicator solution. ^{*b*}15 mg of catalyst was used. ^{*c*}27 mg of catalyst was used. ^{*d*}A much-higher amount of Au NPs was needed to generate enough H₂O₂ to be detectable by the colorimetric titration. ^{*e*}The reaction was conducted for 6 h.

Interestingly, the H₂O₂-generation activity of **Pd@UiO-66-NH**₂ slowly degraded over time:⁴⁹ the composite catalyst was only half as active after 3 cycles (SI, Figure S11). Consistent with this behavior was the slight decrease in the H₂O₂productivity exhibited by **Pd/UiO-66-NH**₂ after being exposed to an H₂O₂-solution at room temperature for 6 h (cf. Table 2, entry 5 and SI, Table S4, entry 4). As the amount of Pd NPs loss after reaction was minimal (~0.2 wt % loss after the 2nd and 3rd cycles; see SI, Table S10), we attributed the activity loss to a decrease in active surface sites of the Pd NPs.

Although the encapsulated metal NPs can generate H_2O_2 from H_2 and O_2 gases, they can also cause its decomposition (Scheme 1), either through a side reaction with the H_2 gas^{47,50}

or by direct decomposition on the surface of the NPs.⁵⁰ These decomposition processes can be quite significant in solution, particularly for batch processes: when the Pd@UiO-66-NH₂ catalyst was employed in the H₂O₂-generation experiment for 6 h, instead of our standard 1 h experiment, the measured level of H₂O₂ productivity dropped by 20 times (Table 2, cf entries 4 and 8). Similar results were observed for Pd/UiO-66-NH₂ (cf Table 2, entry 5 and SI, Table S4, entry 3). Partially supporting the hypothesis that H₂O₂ can also undergo decomposition on the surface of the NPs was the observation that a commercial H₂O₂ solution undergoes more decomposition when being exposed to the Pd/UiO-66-NH₂ in comparison to UiO-66-NH₂ (SI, Table S3, cf entries 2 and 3). These observations reinforce the necessity for positioning the (sal)Mo moiety in close proximity to the NP catalyst: the generated H_2O_2 is most efficiently used for the next step in situ before the decomposition.

Activities of (sal)Mo-functionalized catalysts for alkene oxidation. As expected, our (sal)Mo-functionalized MOF composites were active towards the catalytic epoxidation of cis-cyclooctene with aqueous H₂O₂. In a 70:30 v/v methanol/water media, the same solvent mixture used in the H₂O₂ generation, UiO-66-(sal)Mo successfully produced cyclooctene oxide as the only oxidation product from ciscyclooctene and H₂O₂. Unfortunately, when the reaction time was lengthened from 6 to 18 h, the oxidation productivity decreased (Table 3, cf entries 3 and 4). ICP-OES analysis of the reaction solution after 6 h, where H₂O₂ is still present based on a colorimetric strip test, showed significant leaching (~80%) of Mo from the support (SI, Table S10, entry 4), which could contribute to the observed loss in activity and a lower productivity overtime. However, a separate control experiment where UiO-66-(sal)Mo was exposed to a 70:30 v/v methanol/water solution of cis-cyclooctene over 6 h without stirring showed only 17% loss of Mo content (SI, Tables S6, entry 2), suggesting that the solvent system alone does not cause significant decomposition of the (sal)Mo moiety. Addition of H_2O_2 to the filtrate of this solution results in minimal per-Mo oxidation productivity compared to the UiO-66-(sal)Mo (SI, Table S6, cf. entries 1 vs 2), suggesting that the leached Mo species is not as active as the supported (sal)Mo moieties.

Table 3. The Oxidation of Cis-Cyclooctene with H_2O_2 in 70:30 v/v Methanol/Water^c

| | + H ₂ O ₂ | Catalys CH ₃ OH/H ₂ | t O, rt | o |
|-------|---------------------------------|--|-------------|--|
| Entry | Catalyst | Amount (mg) | Time (h) | Oxidation ^a productivity ^b (mmol/h/kg _{cat}) |
| 1 | - | 0 | 18 | 0 |
| 2 | UiO-66-NH ₂ | 15 | 6 | 0 |
| 3 | UiO-66-sal(Mo) | 15 | 6 | 25 ± 2.5 |
| 4 | UiO-66-sal(Mo) | 15 | 18 | 18 ± 2.5 |

Reaction conditions: *cis*-cyclooctene (0.06 mmol), 30 wt% H_2O_2 (0.06 mmol), CH₃OH (7 mL), and H_2O (3 mL). "Productivity of epoxide was determined by GC-FID against an internal standard." ^bThe error bar was calculated based on the average of standard deviation from all runs. "For additional yield and conversion data, see SI, Table S5.

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Together, the aforementioned data support the hypothesis that the loss of Mo species from the (sal)Mo-functionalized MOF is a primary cause for the deactivation of the epoxidation catalyst. This loss is most likely due to the presence of H_2O_2 , although stirring may also accelerate the leaching by breaking up some of the more-fragile MOF crystals. As these complications would decrease the overall epoxide productivity in our systems, comparison of catalytic capabilities among the catalysts in this study are best made when the losses of Mo are similar. As expected, no epoxide was observed with the parent **UiO-66-NH**₂ MOF (Table 3, entry 2). Given that our MOF-supported NPs and (sal)Mo catalyst components are capable of carrying out their respective catalytic functions at room temperature, we proceeded to elucidate their combined effect in the tandem reaction 1 (Scheme 1).

Activities and Selectivities of MOF-based catalysts in tandem reaction. To minimize catalyst deactivation while still being able to obtain a detectable amount of epoxide, the tandem reaction 1 (Scheme 1) was first carried out using a physical mixture of MOF-supported NPs and (sal)Mo in the batch reactor. In addition, we selected 5-bromo-1-cyclooctene (Br-COE, smallest dimension ~5.23 Å, SI, Section S6) and 4methylstyrene (smallest dimension ~4.22 Å, SI, Section S6) as the alkene substrates to test the hypothesis that the pore aperture of UiO-66-NH₂ (~6 Å⁴¹) can exclude the larger alkene from coming to contact with the encapsulated NPs in MOFs. These substrates were also selected because their hydrogenated products have low volatility, thus minimizing the loss of these alkane byproducts during reactor sampling and allowing for more-accurate analysis of the hydrogenation pathway.

As expected, subjecting Br-COE to our catalytic conditions in the presence of the [Pd@UiO-66-NH₂ + UiO-66-(sal)Mo] catalyst combination, where Pd NPs are encapsulated within the MOF crystals, afforded a product mixture with a low molar ratio of hydrogenation and oxidation products (Hy/Ox) (Table 4, entry 1). In contrast, the $[Pd-PVP/UiO-66-NH_2 +$ UiO-66-(sal)Mo] combination, where the Pd NPs mostly resided on the surface of MOF crystals, yielded a product mixture with a 6-fold higher Hy/Ox ratio (Table 4, entry 2). Given the similar oxidation productivities for these two cases (Table 4, cf entries 1 and 2), the lower Hy/Ox product ratio observed for the first can be attributed to the ability of the UiO-66 pore aperture in selectively sieving out Br-COE and preventing it from coming into contact with the encapsulated Pd NPs inside the Pd@UiO-66-NH₂ crystals. Not surprisingly, this low Hy/Ox ratio was preserved when the dually functionalized Pd@UiO-66-(sal)Mo MOF catalyst was used (Table 4, cf entries 1 and 3).

Table 4. Hy/Ox Ratios and Ox Productivities for Br-COEin the Presence of Different Types of MOF Catalysts



| Entry | Catalyst | Hy/Ox^a ratio ^b | Oxidation (Ox) ^{<i>a</i>} productivity ^{<i>c</i>} (mmol/h/kg _{NPs}) |
|-------|---|---------------------------------|--|
| 1 | Pd@UiO-66-NH ₂ + UiO-66-(sal)Mo | 0.91 ± 0.28 | 191 ± 48 |
| 2^d | Pd-PVP/UiO-66-NH ₂ + UiO-66-(sal)Mo | 5.5 ± 1.7 | 211 ± 48 |
| 3 | Pd@UiO-66-(sal)Mo | 0.94 ± 0.29 | 206 ± 48 |

Reaction conditions: 5% H₂/CO₂ (250 psig), 25% O₂/CO₂ (100 psig), Br-COE (0.05 mmol), CH₃OH (14 mL), and H₂O (6 mL). The catalyst comprises 0.51 mg of NPs and 4.8 mg of Mo by weight. ^aThe oxidation (Ox) product comprises epoxiderearranged compounds and was determined by GC-FID with an internal standard method. ^bThe error bar was proportionally calculated as a percentage of the Hy/Ox ratio based on the average of the percentage standard deviations from the alkane. ^cThe error bar was calculated based on the average of standard deviations from all tries. ^dFor this experiment, Pd-PVP/UiO-66-NH₂ was selected because most of its Pd NPs are located on the exterior surface of MOF crystal, which will provide the best contrast against the Pd@UiO-66-NH₂ in entry 1. For differences in the Hy/Ox ratios between the Pd/UiO-66-NH₂ and Pd-PVP/UiO-66-NH₂ systems, see SI, Table S9.

Further supporting the aforementioned size-selective properties of the UiO-66 support is the much smaller (~1.3 fold) difference in Hy/Ox product ratios observed for 4-methylstyrene when being exposed to the [Pd@UiO-66-NH₂ + UiO-66-(sal)Mo] and [Pd-PVP/UiO-66-NH₂ + UiO-66-(sal)Mo] catalyst combinations, respectively (Table 5, cf. entries 1 and 2). While the encapsulated Pd NPs in the first catalyst combination are still less accessible to the 4-methylstyrene substrate, the smaller size of this alkene would diminish the difference in substrate accessibilities between the two catalyst combinations, especially under similar oxidation productivities.

Table 5. Hy/Ox Ratios and Ox Productivities for 4-Methylstyrene in the Presence of Different Types of MOF Catalysts

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Reaction conditions: 5% H₂/CO₂ (250 psig), 25% O₂/CO₂ (100 psig), 4-methylstyrene (0.05 mmol), CH₃OH (14 mL), and H₂O (6 mL). The catalyst comprises 0.68 mg of NPs and 4.8 mg of Mo ^aThe oxidation (Ox) product comprises epoxideby weight. rearranged compounds (4-methylphenylacetaldehyde, 4methylacetophenone, and minor epoxide ring-opening compounds) as well as other styrene-based oxidation products (4methylbenzaldehyde) and was determined by GC-FID with an internal standard method. While the epoxide is not directly observed given the protic nature of the solvent mixture, the major rearranged products were verified as derivable from the epoxide by an independent experiment (Section S2 in the SI). ^bThe error bar was proportionally calculated as a percentage of the Hy/Ox ratio based on the average of the percentage standard deviations from the Ox products. ^cThe error bar was calculated based on the average of standard deviations from all runs. dFor this experiment, Pd-PVP/UiO-66-NH₂ was selected because most of its Pd NPs are located on the exterior surface of MOF crystal, which will provide the best contrast against the Pd@UiO-66-NH₂ in entry 1. For differences in the Hy/Ox ratios between the Pd/UiO-66-NH₂ and Pd-PVP/UiO-66-NH₂ systems, see SI, Table S9.

It is worth noting that that the similar oxidation productivities for all the catalyst combinations in Table 4 can be attributed to a combination of two factors: the alkene oxidation step being rate-limiting and the low reactivity of the Br-COE substrate. Both of these can be inferred from the much larger H_2O_2 productivities (Table 2, unit = mol/h/kg_{NPs} = 31.2 × mol/h/kg_{cat} for Pd@UiO-66-NH₂)) in comparison to the epox-

idation productivities for UiO-66-(sal)Mo (Table 3, unit = mmol/h/kg_{cat} = $0.16 \times \text{mmol/h/kg}_{Mo}$) and those from the tandem reaction (Table 4, unit = $mmol/h/kg_{NPs}$). While the (sal)Mo moieties in the dually functionalized catalyst may experience a higher local H₂O₂ concentration by being close to the encapsulated Pd NPs, this advantage is greatly diminished if Br-COE is not converted to the epoxide fast enough. As a result, the oxidation productivities for all three-catalyst combinations do not appear to greatly differ, with most of the generated H₂O₂ diffusing into the solution. Together, these observations underline the importance of properly matching the rates of the different active sites in our tandem catalyst. This concept is demonstrated in the next section, where we employ the more-reactive substrate cis-cyclooctene to better accentuate the difference between the dually functionalized catalyst and the physical mixtures of the two singly functionalized catalysts.

The advantages of coupling NP and molecular catalysts on the same MOF microcrystal. To maximize the capability of our dually functionalized catalyst for epoxide generation, the tandem reaction 1 (Scheme 1) was carried out with ciscyclooctene, which is more reactive than both Br-COE and 4methylstyrene in epoxidation and whose epoxide is also more stable than the corresponding epoxides of both of these substrates. As anticipated, the singly functionalized catalyst controls do not show any cyclooctene epoxidation activity under our tandem reaction conditions (Table 6, entries 1-3 and 6). In addition, the absolute values for cis-cyclooctene oxidation productivities by Pd@UiO-66-(sal)Mo and the [Pd@UiO-66-NH₂ + UiO-66-sal(Mo)] physical mixture (Table 6, entries 5 and 4) are higher than the corresponding data for both 4methylstyrene (Table 5, entries 3 and 1) and Br-COE (Table 4, entries 3 and 1), confirming that it is a much better substrate for H₂O₂ utilization.

Consistent with the results shown in Table 5, Pd@UiO-66-(sal)Mo exhibited higher oxidation productivity (~1.5 times) for *cis*-cyclooctene in comparison to the $[Pd@UiO-66-NH_2 +$ UiO-66-sal(Mo)] physical mixture (Table 6, cf entries 5 and 4). This data reinforces our initial hypothesis that the close proximity of two catalysts increases product ratio in the tandem reaction: the closer the two catalysts, the higher the concentration of H₂O₂ around the sal(Mo) groups and the more effective the epoxidation. Because H₂O₂ is generated within the MOF crystal, as it diffuses out it is more likely to be consumed by the (sal)Mo moieties on the crystal surface to produce the epoxide. Similar observations have recently been reported by Yamashita and coworkers for a Pd@Ti-HSS yolkshell nanostructured catalyst used in a tandem H2O2generation/sulfide oxidation reaction.⁵¹ While the alkene oxidation step is still rate-limiting for Pd@UiO-66-(sal)Mo, the (sal)Mo moieties can epoxidize the more-active ciscyclooctene substrate faster, leading to a more effective usage of the H₂O₂ oxidant compared to that in the Br-COE case.

The advantage of having the Pd NPs completely encapsulated inside the UiO-66 crystal is also quite clear. Pd@UiO-66-(sal)Mo afforded a more effective utilization of the generated H_2O_2 oxidant than Pd/UiO-66-(sal)Mo, as reflected by the larger oxidation productivity (Table 6, cf entries 5 and 8) under similar H_2O_2 generation per kg_{NPs} (Table 2, cf entries 4 and 5). Presumably, much of the H_2O_2 that was generated by the Pd NPs that reside on the surface of the Pd/UiO-66-(sal)Mo microcrystals would diffuse away before having a chance to react with the (sal)Mo moiety and the alkene substrate. In

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While employing *cis*-cyclooctene as a substrate can lead to improved usage of the H₂O₂ oxidant, Pd@UiO-66-(sal)Mo is still only ~1.5 times better than the $[Pd@UiO-66-NH_2 + UiO-$ 66-sal(Mo)] physical mixture in oxidation productivities (Table 6, cf entries 5 and 4). This small difference may be explained if the Pd NPs are producing H₂O₂ at a faster rate than can be efficiently consumed by the (sal)Mo catalysts and most of the H₂O₂ would diffuse into the solution. In such a scenario, a major portion of the oxidation product would come from the interactions of the (sal)Mo with the H₂O₂ in solution and the oxidation productivities of the two aforementioned catalysts would not be very different. Employing a slower H₂O₂generating catalyst, such as that based on Au NPs (Table 2, cf entries 5 and 7), should then allow for a more-even matching of the two reactions in our tandem reaction 1 (Scheme 1), resulting in a bigger difference in epoxide productivities between the dually functionalized catalyst and the physical mixture of two singly functionalized catalysts.

 Table 6. Oxidation Productivity for Cis-Cyclooctene in the

 Presence of Different Types of MOF Catalysts^d

| H ₂ + O ₂ + | \bigcirc | Catalyst | |
|-----------------------------------|------------|----------|----|
| | | 0 | Ox |

| - | | Catalyst | NPs | Mo | $\mathbf{O}\mathbf{x}^a$ productivity ^b |
|---|-------|---|------|------|--|
| | Entry | | (| (| (mm al/h/lag) |
| _ | - | | (mg) | (mg) | $(\text{mmol/n/kg}_{\text{NP}})$ |
| _ | 1 | - | - | - | 0 |
| | 2 | UiO-66-sal-Mo | - | 4.8 | 0 |
| | 3 | Pd@UiO-66-NH ₂ | 0.5 | - | 0 |
| | 4 | Pd@UiO-66-NH ₂ + UiO-66-sal(Mo) | 0.5 | 4.8 | 570 ± 64 |
| | 5 | Pd@UiO-66-sal(Mo) | 0.5 | 4.8 | 828 ± 64 |
| | 6 | Pd/UiO-66-NH ₂ | 0.5 | - | 0 |
| | 7 | Pd/UiO-66-NH ₂ + UiO-66-sal(Mo) | 0.7 | 4.8 | 493 ± 120 |
| | 8 | Pd/UiO-66-(sal)Mo | 0.7 | 4.8 | 599 ± 120 |
| _ | 9 | Au/UiO-66-NH ₂ | 2.6 | - | 2 ± 0.24^{c} |
| | 10 | Au/UiO-66-NH ₂ + UiO-66-sal(Mo) | 2.6 | 9.6 | 2.5 ± 0.24 |
| | 11 | Au/UiO-66-(sal)Mo | 2.6 | 9.6 | 26 ± 0.24 |

Reaction conditions: $5\% \text{ H}_2/\text{CO}_2$ (250 psig), $25\% \text{ O}_2/\text{CO}_2$ (100 psig), *cis*-cyclooctene (0.12 mmol), CH₃OH (14 mL), and H₂O (6 mL). ^{*a*}Amount of products and productivity were determined by GC-FID against an internal standard. ^{*b*}The error bar was calculated by averaging standard deviations from all tries for each catalyst system. ^{*c*}While a small amount of cyclooctene oxide can be observed in the presence of the **Au/UiO-66-NH**₂ control, this is not surprising because Au NPs are known to be active for alkene epoxidation with O₂ and TBHP.⁵²⁻⁵³ ^{*d*}See SI, Table S9 for a full

set of data that includes the Pd-PVP system and the **Hy/Ox** ratios for all four tandem catalyst systems in this study.

Indeed, the advantage of coupling two catalysts in one MOF crystal is most noticeable when comparing Au/UiO-66-(sal)Mo and [Au/UiO-66-NH₂ + UiO-66-(sal)Mo] (Table 6). The dually functionalized catalyst exhibited an epoxide productivity that is an order of magnitude higher than the corresponding physical mixture (Table 6, cf entries 10 and 11). We attribute this large difference in epoxide productivities observed between the two Au NP-containing catalysts to the slower production of H₂O₂ by Au NPs. As the amount of H₂O₂ being generated in Au/UiO-66-(sal)Mo is smaller than that in the Pd analog, the oxidant should have a better chance of reacting with the (sal)Mo catalyst moiety on the surface of the MOF crystal before diffusing into the solution. In contrast, in the [Au/UiO-66-NH₂ + UiO-66-sal(Mo)] physical mixture, the small amount of H₂O₂ being generated by Au/UiO-66-NH₂ must additionally diffuse into solution before reaching the UiO-66-sal(Mo) catalyst, leading to a large decrease in the effective usage of the oxidant in the epoxidation step.

The aforementioned close-proximity effect, which is much larger for the two Au/UiO-66 systems (10×; Table 6, cf entries 10 and 11) compared to that for the analogous Pd/UiO-66 systems (1.2×; Table 6, cf entries 7 and 8), can indeed be attributed to the large differences in rate of H₂O₂ generation. As the Pd NPs produces H₂O₂ at a faster rate than Au NPs (Table 2, cf entries 5 and 7), a large portion of the generated H₂O₂ diffuses into the solution, leading to a smaller percentage difference in the oxidant concentrations around the (sal)Mo moiety in Pd/UiO-66-(sal)Mo compared to that in the [Pd/UiO-66-NH₂ + UiO-66-sal(Mo)] physical mixture. This in turn leads to a smaller percentage difference in the two corresponding epoxide productivities.

In summary, we have demonstrated that the controlled positioning and coupling of two different catalysts in one MOF microcrystal can be highly beneficial for the tandem H₂O₂generation/alkene-oxidation reaction (Scheme 1, Eq. 1). By encapsulating NP catalysts inside UiO-66-NH₂ microcrystals, we minimize their interactions with the large alkene substrates and reduce side reactions such as alkene hydrogenation in the presence of H₂. In addition, enhanced epoxide productivity is achieved when both the H₂O₂-generating NP and the (sal)Mo epoxidation catalysts are integrated on the same MOF crystal. This colocalization effect can be quite important for the most effective usage of the relatively unstable H₂O₂ oxidant, especially for the case of Au NP, whose H₂O₂-generation activity is lower than that for the Pd NP analogue. Together, these data suggest that the close positioning and good activitymatching between the two active species in the support as well as the substrate are both important for the improvement in tandem catalysis. While such study are beyond the scope of the current manuscript, the use of MOF as a controllable platform for the close co-deployment of different catalysts that can act in concert in a molecular-like scale is a promising venue for integrating biocatalytic concepts into abiotic platform, akin to cascade reactions in multi-enzyme processes.⁵⁴ ⁴⁻⁵⁶ Successful implementation of such a concept can allow for the spatial separation of incompatible reactants⁵⁷, allowing for the development of novel tandem reactions with high selectivity and efficiency.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10/1021/

General information concerning materials and methods; procedures for the syntheses of the MOF catalysts; additional discussions; PXRD patterns, N₂ isotherms, and catalysis data (PDF).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

MOF, metal-organic frameworks; BET, Brunauer–Emmett– Teller; PXRD, powder X-ray diffraction; ICP-OES, inductively coupled plasma optical emission spectrometry.

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