

Probing the Interface between Encapsulated Nanoparticles and Metal–Organic Frameworks for Catalytic Selectivity Control

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desired crotyl alcohol. This work provides a spectroscopic protocol to study hybrid interfaces and sheds light on their design for effective NP-MOF catalysts.

ontrolling the catalytic performance of metal nanoparticles (NPs) is a longstanding research topic in heterogeneous catalysis because they are at the center of many key industrial processes.¹⁻³ Within this field, expanding and improving selectivity remains one of the most challenging aims. It is well-known that selectivity can be influenced by reaction conditions, NP sizes, and NP compositions,⁴ but a molecularlevel design of selectivity control remains elusive. More recently, introducing organic ligands to the NP surface has proved to be an effective way to rationally tune selectivity by directing intermediates on a molecular level,⁵ and numerous organic ligands have been applied to effectively control the selectivity.⁶⁻⁹ Recently, intermediate control has been extended from surface adsorbed ligands to crystalline solids, metal-organic frameworks (MOFs).¹⁰ The crystalline nature of the frameworks prevents the transient structure of the organic ligands that could be a potential issue during certain catalytic reactions.¹¹ Selectivity for a great number of important reactions has indeed been demonstrated using MOFs as intermediate-directing agents, such as the selective hydrogenation of α , β -unsaturated aldehydes, the selective oxidation of diols, and the isomerization of methylcyclopentane.¹²⁻¹⁹ Even the challenging selective hydrogenation of acrolein has been demonstrated, which has never been reported using organic ligands alone.²⁰

The superior selectivity control provided by MOFs can be understood through the underlying mechanisms. The intermediate-directing agents control selectivity by modifying the electronic structure of NPs or directing the conformation of intermediates.²¹ For example, in α , β -unsaturated aldehyde hydrogenation, both adsorbed ligands and coated MOFs on the catalytic surface can generate steric effects to prevent intermediates lying down in a flat conformation, allowing only the terminal C=O bond to be hydrogenated and leading to high chemoselectivity for unsaturated alcohol.^{9,15} The crystalline nature of MOFs could further provide a more uniform steric control to direct intermediates at the interfaces between NPs and MOFs.²² The tunable nature of MOFs allows this steric control to be fine-tuned.²³

Based on this mechanism of intermediate directing, the detailed structure at the interface is very important. In order for the steric effect of the MOF pores to direct the intermediate for selectivity control, the MOF must be directly coated on the metal surface without any gap or chemicals in between (Scheme 1 and notes in the Supporting Information, SI). However, this important feature has been overlooked in many previous works. Only a well-defined and direct interface

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Scheme 1. Schematic Illustration of the Possible Intermediate Conformation at the Interface^a



^{*a*}(a) Ordinary intermediate conformation on a pure metal surface. (b) Conformation directed by a direct NP–MOF interface. (c) Conformation poorly controlled by an ill-defined NP–MOF interface. A crotonaldehyde molecule was used as a model reactant. These possible conformations are adopted from the DFT literature references.^{24,31}.

between NPs and MOFs could provide selectivity control.^{24–26} In this work, we aim to probe the interfacial structures and their impact on selectivity control. We first generate NP–MOF interfaces by three commonly used approaches, impregnation, coating, and one-pot.^{27–30} Then, we use infrared and Raman spectroscopy to gain chemical information at the interface generated by each approach. After understanding the interface, we tested the selectivity of the catalysts for a model reaction, the hydrogenation of an α , β -unsaturated aldehyde.

As mentioned, the three methods used to form NP@MOF catalysts are impregnation, coating, and one-pot. In the impregnation method, MOFs are synthesized first and serve as a matrix to immobilize metal precursors that are reduced to form encapsulated NPs.³² In the coating method, colloidal metal NPs are synthesized first and then introduced into an MOF growth solution to coat MOF on the NPs.³³ In the onepot method, metal NPs and MOF precursors are mixed in one pot and then heated to form metal NPs and simultaneously coat MOF. These three methods all generate an NP-MOF interface; however, we hypothesize that their detailed interfacial structure could vary due to differences in their formation process (Scheme 2). The impregnation method is the most conventional way to make heterogeneous catalysts. It could generate a direct NP-MOF interface, but it is challenging to completely avoid the growth of NPs on the external surface of the preformed MOFs. In addition, the size of formed NP is less tunable, as most of the previous methods could only generate NPs with small size (Scheme 2a).^{15,34} For the coating method, because MOFs form around presynthesized NPs, the colloidally synthesized NPs could be of welldefined morphologies and compositions. However, the capping agent used to stabilize colloidal NPs and provide an anchor for MOF growth could be trapped at the interface, preventing direct interaction between the NP and the MOF (Scheme 2b). For the one-pot method, it has a great potential to form direct interfaces because no capping agent is added (Scheme 2c); however, the synthetic condition of this relatively new method is not fine-tuned for the interface control.³⁵ These hypothesized differences motivated us to perform a detailed study to provide direct comparisons between the methods.

Chemically stable UiO-66-NH₂ (University of Oslo-66-NH₂) is selected as the host MOF for this study.³⁶ UiO-66-NH₂ is formed by the assembly of zirconium clusters and 2-aminoterephthalic acid (BDC-NH₂). The amino group has a

Scheme 2. Schematic Illustration of Three Different Approaches to Form the NP@MOF Catalyst^a

(a) Impregnation Method



a'(a) Impregnation, (b) coating, and (c) one pot. The illustrated sizes of the NPs in the scheme are used to emphasize the differences between the methods.

high affinity to metal NPs^{37–39} and also provides a probe for later spectroscopic study.^{15,37} We used the reported methods for the encapsulation of Pd NPs in UiO-66-NH₂ to generate the impregnation and coating samples (details in the SI; Figures 1a,b and S1).^{15,39–41} Because there is no reported onepot method for NP@UiO-66-NH₂, we have developed a method modified from previous reports for NP@UiO-66.³⁵ In a typical experimental condition, metal precursors (salts of sodium tetrachloropalladate) and MOF precursors (zirconium



Figure 1. Characterization of NP@UiO-66-NH₂. TEM images of Pd@UiO-66-NH₂ generated by (a) impregnation, (b) coating, and (c) one-pot methods. TEM images of Pt@UiO-66-NH₂ generated by (d) impregnation, (e) coating, and (f) one-pot methods. See the Supporting Information for the loading and size distribution of the encapsulated NPs.

tetrachloride and BDC-NH₂) are mixed in the solvent. The solution is kept at 120 °C for 24 h without stirring. Pd NPs form within the first 15 min of heating, followed by the formation of UiO-66-NH₂ (Figure S2). Uniform Pd@UiO-66-NH₂ nanocrystals were produced (Figure 1c). Powder X-ray diffraction (PXRD) patterns of Pd@UiO-66-NH₂ composites show no difference compared to simulated UiO-66 (Figure S3). The presence of metal salts does not affect MOF formation (Figure S4). The loading of Pd in Pd@UiO-66-NH₂ was identified by inductively coupled plasma optical emission spectrometry (ICP-OES) as 3.0 wt %.

Although the newly developed one-pot synthesis is not the focus of this work, we want to emphasize its advantages, primarily its potential to form controlled NP-MOF interfacial structures. The procedure has improved upon previously reported one-pot methods through the use of BDC-NH₂, which plays two roles here. First, BDC-NH₂ can promote the formation of NP nuclei and accelerate the formation of NPs.⁴² Second, its affinity for metals allows it to stabilize the metal surface and prevent NP aggregation without additional capping agents. The BDC-NH₂ stabilized NPs are thus formed first and then encapsulated into MOFs (Scheme 2c). When native BDC is used as the MOF linker under the same reaction conditions, the synthesized NPs formed a series of aggregates outside of the UiO-66 crystals (Figure S5). Using BDC-NH₂, the size and composition of encapsulated NPs can further be easily tuned by changing the reaction temperature and metal precursor(s), respectively. At higher temperatures, the nucleation rate is accelerated, leading to smaller particles. Pd NP sizes can be tuned from 3.6 \pm 1.0 nm to 9.9 \pm 1.8 nm by decreasing the synthesis temperature from 150 °C to 90 °C (Figures S6 and S7). PdPt alloy NPs were used to demonstrate composition control. When a mixture of Pd and Pt precursors were introduced (details in the SI), a series of alloyed NPs formed (Figures S8). A volcano relationship between the activity and the Pd:Pt ratio was observed (Figures S9 and Table S1), indicating that the encapsulated metal NPs are indeed alloyed.43 A linear relationship was observed while using a mixture of pure Pt and Pd NPs (Figure S10).

Before studying the interfacial structures generated by the three different methods, we tested whether the metal NPs are encapsulated by carrying out size-selective alkene hydrogenation, using ethylene, cyclohexene, and cyclooctene, and comparing the results with a control sample, in which NPs are on the external surface of UiO-66-NH₂. The loading and size distribution of encapsulated Pd NPs in each sample are summarized in Table S2 and Figure S11. Due to the smaller size of the NPs formed in the impregnation sample,^{15,34} the metal NP surface areas of the four samples were normalized through a standard method of ethylene hydrogenation (to 40% conversion, Table S3).44 Because the MOF aperture size is bigger than the cyclohexene and smaller than cyclooctene, we observe low activity for cyclooctene hydrogenation over impregnation, coating, and one-pot samples (Figure 2), while the control sample (Pd-on-MOF) shows high activity for both cyclohexene and cyclooctene hydrogenation. This result indicates that most of the metal NPs are indeed encapsulated. Because we used the impregnation method, the higher activity of cyclooctene hydrogenation could be related to NPs on the external surface, which has been reported.⁴⁵ It is worth mentioning that these NPs on the external surface of MOFs can be avoided when extra synthetic steps were introduced.⁴⁵

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Figure 2. Size-selective alkene hydrogenation over Pd NPs on UiO-66-NH₂ and Pd@UiO-66-NH₂ obtained using the coating, one-pot, and impregnation methods. The catalyst activity was normalized by ethylene hydrogenation held at 40% conversion. Ethylene hydrogenation is run at 0 °C, cyclohexene hydrogenation is run at 25 °C, and cyclooctene hydrogenation is run at 40 °C.

After investigating the encapsulation of NPs into MOFs, we next studied the NP-MOF interfacial structure. Although the structures look similar under TEM and identical under XRD, these characterizations method provide little insight into the interfacial structure (Figure 1). In light of this, the formation of chemical interactions at the interface was investigated through IR and Raman spectroscopy. Different NP-MOF interfacial structures lead to different chemical bonding between NP and MOF. These chemical interactions can be probed by measuring changes in the chemical properties of either the MOF linkers or the NP surface. To study change in the MOF linkers after the formation of NP-MOF, we used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to monitor the stretching of the amine group of BDC-NH₂. Interaction between NP and MOF should lead to a weaker N-H bond, resulting in a red-shift of the N-H stretch IR frequency.¹⁵ As shown in Figure 3, four samples were compared: pure UiO-NH₂ and Pd@UiO-NH₂ generated by each of the three methods, impregnation, coating, and one-pot. In the spectra, the bands at 3520 and 3401 cm⁻¹ are attributed to the N-H asymmetric and symmetric stretching vibration peak, respectively, and the band at 3670 cm⁻¹ corresponds to the μ_3 -OH stretching of the zirconium cluster.⁴⁶ The impregnation sample showed the greatest red-shift, indicating that the MOF linkers are chemically interacting with the encapsulated metal NPs. While lesser, the red-shift of the onepot sample also indicates the MOF linkers are chemically interacting with encapsulated NPs. In contrast, no noticeable shift was observed for the coating sample, signifying that there is little interfacial interaction between MOF and NP. We attribute this limited contact to residues trapped at the interface (Scheme 2b), which will be discussed in detail in a later section. The greater shift observed in the impregnation sample indicates that there are more chemical bonds at the NP-MOF interface likely due to the smaller NP size generated by the impregnation method (Figure S10).

To probe changes in the NP electronic structure, we introduced carbon monoxide (CO) as a probe molecule, because the stretching frequency of CO adsorbed on a metal



Figure 3. DRIFTS, with the characteristic stretches of the amine group highlighted, for UiO- NH_2 and Pd@UiO-66- NH_2 obtained using the impregnation, one-pot, and coating methods. Significant shifts in the N–H stretch indicate that the MOF chemically interacts with the Pd surface.

surface is sensitive to the electronic structure of the metal.⁴⁷ The small size of CO further allows it to easily pass through the UiO-66 aperture. For these studies, Pd NPs were replaced by Pt NPs, as the Pt surface yields well-defined (and wellunderstood) CO signals.^{48,49} Pt@UiO-66-NH₂ samples were synthesized via the same routes as Pd@UiO-66-NH₂ (TEM images and PXRD pattern are shown in Figure 1d-f and Figure S12, respectively).^{15,40} The loading and size distribution of encapsulated Pt NPs in each sample are summarized in Table S2 and Figure S13. The more bonds formed at the NP-MOF interface, the more red-shifted the CO stretch frequency, as the electron-donating amine group increases the charge density on the metal surface, resulting in increased electron back-donation to CO antibonding orbitals, weakening the CO bond.⁵⁰ As shown in Figure 4, four samples were again compared: Pt NPs-on-SiO₂, as the control, and Pt@UiO-66-NH₂ synthesized using the impregnation, coating, and one-pot methods. In the spectra, the band between 2050 and 2100 cm⁻¹ is attributed to CO linearly bound on Pt atoms (CO_{atop}).⁴⁷ The frequency of CO_{atop} in the Pt-on-SiO₂ sample, ~ 2090 cm⁻¹, was used as a reference for comparison.⁴ Compared to this reference frequency, the CO_{atop} frequency of the impregnation sample shows a red-shift from 2090 to 2066 cm⁻¹, further indicating the chemical interaction between the linkers and metals in the impregnation sample. As expected, the one-pot method also shows a similar red-shift ($\sim 20 \text{ cm}^{-1}$) due to the chemical interaction. In contrast, a relatively small red-shift (~8 $\,\mathrm{cm^{-1}})$ of $\mathrm{CO}_{\mathrm{atop}}$ is observed in the coating sample. Similar to the NH₂ stretching study, it implies less chemical interaction at the interface in the coating sample (Scheme 2b). Importantly, this study also suggests that insights provided by the Pd@UiO-66-NH₂ system can be extended to other metal NPs. Next, we studied the mechanisms causing the differences in NP-MOF interactions.

Capping agents are used to stabilize NPs for colloidal synthesis. 51,52 We hypothesize that the capping agents on the



Figure 4. DRIFTS of CO adsorbed on Pt-on-SiO₂ and Pt@UiO-66-NH₂ obtained using the impregnation, one-pot and coating methods. Significant shifts in CO_{atop} indicate that the MOF chemically interacts with the Pt surface, changing the electronic structure of Pt.

surface of colloidal NPs are trapped at the interface after MOF coating. These trapped organic ligands block the chemical interaction between the MOF and the NP, generating an ill-defined interface. To test this hypothesis, we used Raman spectroscopy to investigate the interfacial capping agents. The same coating method and capping agent, polyvinylpyrrolidone (PVP), were used, but the metal NPs were switched to Au for its surface enhancement (details in the SI, Figures S14–16).⁵³ Because the surface plasmon resonance of the Au NPs largely promotes the Raman signal of molecules close to the Au surface, the information is very interface specific.⁵⁴ As shown in Figure 5a, the noncoated Au-PVP NPs showed a band at 1530



Figure 5. (a) Raman spectra of Au-PVP NPs, UiO-NH₂, and Au@ UiO-66-NH₂ formed using the coating method. (b) Ethylene hydrogenation over Pt@UiO-66-NH₂ obtained using the one-pot and coating methods. Ethylene hydrogenation is run at 0 °C.

cm⁻¹, corresponding to stretching vibrations of the C=O moiety on PVP, in agreement with the literature.⁵⁵ After coating with UiO-66-NH₂, which has no characteristic peaks in this region, the peak can be clearly seen. The presence of the PVP signal in the composite suggests that the capping agents used to stabilize colloidal metal NPs are indeed trapped inside the coated MOF. In contrast, no PVP signal was observed for the samples generated by impregnation and one-pot methods

(Figure S17). To further examine the influence of this trapped interfacial capping agent, we compared the activity for ethylene hydrogenation of $Pt@UiO-66-NH_2$ synthesized by the coating and one-pot methods with similar Pt loading and particle size. (The NP sizes generated by the impregnation method cannot be controlled, so it was excluded from this study.) As shown in Figure Sb, the coating sample shows a much lower activity than the one-pot sample, which is attributed to active site blocking by PVP residues.^{56,57}

After gaining an initial understanding of the NP-MOF interfacial structure, we carried out a model reaction, crotonaldehyde hydrogenation (Figure 6a). Numerous studies



Figure 6. (a) Two pathways for the hydrogenation of crotonaldehyde. (b) Selectivity for crotonaldehyde hydrogenation over Pt NPs on UiO-66-NH₂ and Pt@UiO-66-NH₂ obtained using the coating, impregnation, and one-pot methods. To compare the selectivities of our samples, the conversion of each reaction was kept at 30%. Crotyl alcohol is the preferred product, and selectivity was determined by its ratio to the sum of all three products. Reaction conditions: 2 mL of isopropanol, 100 μ L of crotonaldehyde, 30 bar H₂, 70 °C, and reaction time of 18 h.

suggest that this type of α , β -unsaturated aldehyde hydrogenation over a NP@MOF catalyst favors the hydrogenation of the C==O bond, which is originally thermodynamically less favorable than the hydrogenation of the C==C bond.^{15,16,20,58-61} Although many different mechanisms have been proposed, such as steric¹⁵ or activation effects,²⁰ a direct interface is required for high selectivity in all hypothesized mechanisms (Scheme 1). For example, it has been proposed that the improved selectivity is due to the MOFs ability to regulate the orientation of intermediates.¹⁵ Such regulation is dependent on a clean and direct NP-MOF interface. For our study, Pt@UiO-66-NH₂ was chosen because it produces fewer byproducts than Pd.⁶² To compare the selectivity of our samples, the conversion of each reaction was kept at 30% (Table S4). As shown in Figure 6, four samples were compared: pure Pt NPs on UiO-66-NH₂ and Pt@UiO-66-NH₂ synthesized through the coating, impregnation, and one-

pot methods. The sample of pure Pt NPs on the MOF surface, which serves as a control (Pt-on-MOF), shows a 6.0% selectivity to crotyl alcohol. For the impregnation sample, selectivity increased (42.8%), indicating the promotion of the hydrogenation of C=O due to the presence of a direct NP-MOF interface. However, the sample generated by the coating method shows only a marginal increase in selectivity (9.8%), which is attributed to the ill-defined interface suggested by our spectroscopic studies. The highest selectivity of crotyl alcohol (70.4%) was observed in the one-pot sample, also due to the direct interface revealed by our spectroscopy study. Although both samples have a direct interface, NP size control allows the one-pot sample to show higher catalytic activity than the impregnation samples (Figures S11 and S13). It has been reported that larger Pt NPs promote the formation of unsaturated alcohol.^{63,64} The impregnation method can only generate NPs with a small size that disfavors the formation of unsaturated alcohol.^{15,34} Besides providing a fundamental understanding of the interface, our study also reveals the potential of the one-pot synthesis method when the metallinker interaction is controlled and the formation sequence is regulated. We hypothesize that, if the conditions are optimized, NPs will form first, stabilized by linkers with a high metal affinity. At this stage, the morphology and composition of the NPs can be controlled by colloidal methods because the MOF is not formed yet. Then, the MOF precursors will bond to the linkers on the NP surface and form a MOF around the NPs, forming a clean and direct interface. We believe that this process could lead to highly controlled and active interfacial structures.

In summary, we have developed a spectroscopic protocol to probe the chemical interactions at the interface by combining IR and Raman spectroscopies. We have used this toolbox to reveal differences in the chemical interactions at the interfaces generated by several common synthesis methods. We have found that although the coating method allows for better control over the encapsulated NPs than the impregnation method, the interface generated by the coating approach contains a trapped capping agent. This trapped capping agent reduces crotyl alcohol selectivity for the hydrogenation of crotonaldehyde. Our developed one-pot method, on the other hand, shows the highest selectivity to the unsaturated alcohol, due to the direct NP-MOF interface and size control of the encapsulated NPs. While the encapsulation of metal NPs into MOFs has been shown to be a route to promising composite catalysts, our current study shows that it is essential to finetune the interfacial structures between NPs and MOFs. The toolbox and understanding established in this work could offer a perspective for further optimization of MOF-based heterogeneous catalyst design.

EXPERIMENTAL SECTION

Chemicals and Characterization. See the section of chemicals and characterization details in the Supporting Information for information on instrumentation and the sources of chemicals.

Synthesis of Pd@UiO-66-NH₂ Using the Impregnation Method. See the Supporting Information for the synthesis of encapsulated Pt NPs and Au NPs in UiO-66-NH₂ using the impregnation method. To form Pd@UiO-66-NH₂ composites using the impregnation method, 100.0 mg of activated UiO-66-NH₂ powder (see the Supporting Information for the synthesis of UiO-66-NH₂) was dispersed in 5 mL of dichloromethane followed by sonication for 40 min at room temperature. Then, 5 mL of dichloromethane containing 7.0 mg of palladium acetate was added dropwise to the above solution with magnetic stirring at 900 rpm. The mixture was stirred at 500 rpm for 24 h at ambient temperature. The assynthesized Pd^{2+} -impregnated UiO-66-NH₂ was centrifuged and washed with dichloromethane three times. The sample was further washed by dichloromethane three times every 12 h to remove the remaining palladium precursor adsorbed on the surface of UiO-66-NH₂. The resulting sample was then air-dried and reduced under a 10% H₂ flow (50 mL/min, balanced with helium) at 200 °C for 2 h.

Synthesis of the Pd@UiO-66-NH2 Composite Using the Coating Method. See the Supporting Information for the synthesis of encapsulated Pt NPs and Au NPs in UiO-66-NH2 using the coating method. In general, 25.8 mg of ZrOCl₂·8H₂O (0.08 mmol) and 14.5 mg of BDC-NH₂ (0.08 mmol) were dissolved in 7.622 mL of DMF in a 20 mL scintillation vial, and then 1.378 mL of acetic acid was added into the solution to take the final volume to 9 mL. Next, 1 mL of Pd NPs (0.5 mg/mL in DMF, synthesized from the colloidal method using PVP as capping agents) was introduced into the above solution, and the solution was heated at 120 °C in an oil bath for 2 h (see the Supporting Information for the synthesis of Pd NPs). After cooling, the formed Pd@UiO-66-NH2 powder was collected by centrifugation (8000 rpm, 10 min). The sample was washed with DMF three times. Then, the as-synthesized Pd@UiO-66-NH₂ powder was activated by solvent exchange to remove the residues trapped in the framework. The activation process was carried out by washing three times with DMF and methanol every 12 h.

Synthesis of Pd@UiO-66-NH2 Using the One-Pot Method. See the Supporting Information for the one-pot synthesis of encapsulated Pt NPs, the PdPt alloy, and Au NPs in UiO-66-NH₂ using the one-pot method. In general, 14.5 mg of BDC-NH₂ (0.08 mmol) and 2.78 mg of Na₂PdCl₄·3H₂O (0.008 mmol) were dissolved in 7.622 mL of DMF in a 20 mL scintillation vial, and then 1.378 mL of acetic acid was added into the solution to make the final volume 9 mL. Next, 1 mL of DMF containing 18.6 mg of ZrCl₄ (0.08 mmol) was introduced into the above solution. The solution was heated to 120 °C in an oil bath for 24 h. After cooling, the formed Pd@UiO-66-NH₂ powder was collected by centrifugation (8000 rpm, 10 min). The sample was washed with DMF three times. Then, the assynthesized Pd@UiO-66-NH2 powder was activated by solvent exchange to remove residues trapped in the framework. Activation was performed by washing with DMF and methanol three times every 12 h. The activated Pd@UiO-66-NH₂ sample was dried at 80 °C for 24 h.

DRIFTS Measurement. DRIFTS spectra were collected using a Bruker Tensor 27 with a mercury–cadmium–telluride detector (MCT) and a Harrick diffuse reflectance accessory. The beam alignment and calibration were performed before each measurement. Both CO-DRIFTS spectra and DRIFTS spectra and were carried out using this instrumental setup.

Raman Measurment. Raman spectra were collected on a Micro-Raman system (XploRA, Horiba) with a 532 nm laser excitation at room temperature. Before each measurement, samples were dropcast on a Si wafer (1.0 cm \times 1.0 cm) and dried at 80 °C for 24 h. Considering the sensitivity of the MOFs to laser excitation, a low output power (10 mW) was used to carry out the Raman measurement. The laser alignment and calibration at 532 nm were performed before each measurement using a Si wafer. See the Supporting Information for the detailed procedure.

Alkene Hydrogenation. Samples were diluted with low surface area quartz and loaded into U-shaped glass reactors. The glass reactor was then connected to a home-built gas-phase flow system for alkene hydrogenation. Gas flows, including helium, hydrogen, and ethylene, were regulated using calibrated mass flow controllers. The desired partial pressure of cyclohexene or cis-cyclooctene was achieved by bubbling He through the liquid and assuming saturation. For all the reactions, the gas composition was analyzed with a mass spectroscope (MKS special V2000P). The temperature was controlled by a furnace (CARBOLITE) and PID controller (Diqi-Sense) with a type-K thermocouple. See the Supporting Information for the detailed procedure. **Crotonaldehyde Hydrogenation.** Catalysts were dispersed in 2 mL of isopropanol solution in the 10 mL ampule, and then 40 μ L of crotonaldehyde (0.4 mmol) was added into the above solution. Before catalysis, the high-pressure reactor vessel (Wattacas Inc., 500 mL) was preheated to 70 °C. The temperature was controlled using a hot plate (RCT basic, IKA) with a type-K thermocouple. Subsequently, the ampule was transferred into a high-pressure reactor vessel. The autoclave was purged 5 times with H₂ to remove air. Then, the hydrogenation of crotonaldehyde was carried out at 30 bar H₂ at 70 °C for 18 h with magnetic stirring at 500 rpm. After that, the catalysts were separated by centrifugation, and the reaction solution was filtered through a filter membrane (0.22 μ m). The products were analyzed using gas chromatography–mass spectrometry (Shimadzu QP2010 Ultra, column: Rtx-5, 30 m × 0.25 mm × 0.25 μ m).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c03007.

Detailed experimental procedures, characterizations of the synthesized samples, ICP-OES measurement, Raman study, DRIFTS measurement, alkene hydrogenation, and crotonaldehyde hydrogenation (PDF)

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Notes

The authors declare no competing financial interest.

^{II}Chia-Kuang Tsung died on January 5, 2021, from complications due to COVID-19.

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