Communication

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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.8b04047 • Publication Date (Web): 17 Jun 2018

Aperture-Opening Encapsulation of a Transition Metal Catalyst in a Metal-Organic Framework for CO_2 Hydrogenation

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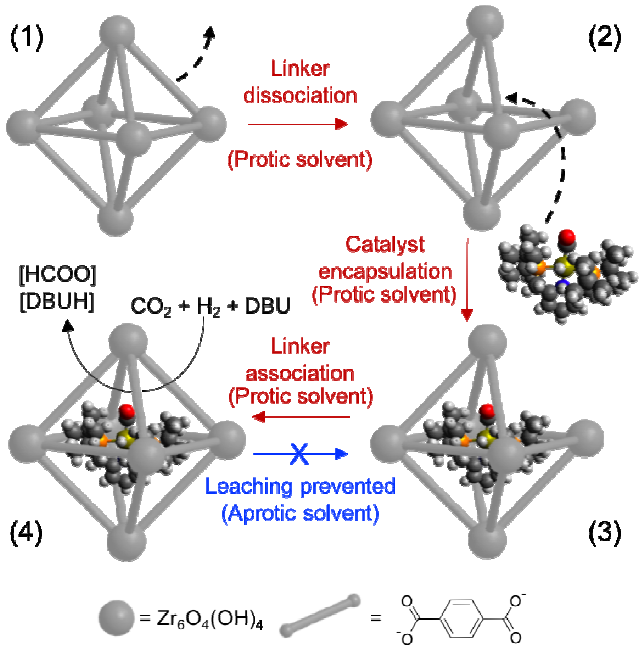
Supporting Information Placeholder

ABSTRACT: The aperture-opening process resulting from dissociative linker exchange in zirconium-based metal-organic framework (MOF) UiO-66 was used to encapsulate the ruthenium complex (^{tBu}PNP)Ru(CO)HCl in the framework (^{tBu}PNP = 2,6-bis((di-*tert*-butyl-phosphino)methyl)pyridine). The resulting encapsulated complex, [Ru]@UiO-66, was a very active catalyst for the hydrogenation of CO_2 to formate. Unlike the analogous homogeneous catalyst, [Ru]@UiO-66 could be recycled five times, showed no evidence for bimolecular catalyst decomposition, and was less prone to catalyst poisoning. These results demonstrated for the first time how the aperture-opening process in MOFs can be used to synthesize host-guest materials useful for chemical catalysis.

Host-guest composites have proven to be a versatile platform for a wide variety of applications including gas storage,[1] drug delivery,[2] chemical sensing,[3] and catalysis.[4] Recently, much attention has been drawn to the utilization of metal-organic frameworks (MOFs) as host materials.[5] MOFs are crystalline coordination polymers that are formed by the self-assembly of organic bridging linkers and metallic nodes used as secondary building units (SBU). The advantage of MOFs as host materials stems from the ability to tune their molecular structure. This versatility has led to a number of methods to construct catalytically active MOF systems, including encapsulation of homogeneous catalysts into MOFs during their synthesis (i.e. *de novo* synthesis),[6] construction of molecular catalysts in the MOF pores after MOF formation (i.e. ship-in-a-bottle synthesis),[7] functionalization of linkers with catalytically competent species,[8] and utilizing the modified MOF nodes as the active sites.[9]

Recently, we have developed a new approach to encapsulate guest molecules into MOFs that circumvents lengthy synthetic sequences and incompatible reaction conditions.[10] In this approach, molecular guests larger than the aperture size of a MOF host are encapsulated into the pores by taking advantage of aperture-opening events that occur as a result of dissociative linker exchange reactions (Scheme 1). In this work, we show that the aperture-opening process exists even in a robust MOF and is highly dependent on the identity of the solvent used,[11] which led us to pursue a unique strategy for using MOFs to synthesize host-guest composites for chemical catalysis (Scheme 1).

Scheme 1



The strategy involves encapsulating catalysts and running catalytic reactions under different conditions. We use solvents that favor dissociative linker

exchange to promote the encapsulation of a molecular complex via aperture-opening events (e.g. (1) to (4), Scheme 1). In contrast, molecular catalyst leaching from the framework during catalysis is prevented by carrying out catalytic reactions in solvents where dissociative linker exchange is slow (e.g. (4) to (3), Scheme 1). Herein, the successful implementation of this strategy is demonstrated for the first time with the encapsulation of a highly active homogeneous CO_2 hydrogenation catalyst[12] into the robust metal-organic framework, UiO-66.[13] The encapsulated catalyst exhibited properties that were hybrid between homogeneous and heterogeneous catalysts, and evidence is provided that demonstrates that the majority of the active catalyst was encapsulated inside of the MOF rather than on its surface.

We anticipated that the robust UiO-66 would be compatible with a variety of reaction conditions. As a result, UiO-66 was selected as the host material to demonstrate the concept. In order to verify that the aperture-opening events in UiO-66 can be used to encapsulate guests similarly to what we have observed in ZIF-8,[10] the fluorescent dye Rhodamine 6G (R6G) was used as a model guest molecule (see SI for detailed experiments). Dye encapsulation was observed when UiO-66 was suspended in protic polar solvents (Table S1), and encapsulation of R6G was depressed when exogenous terephthalic acid was present (Figure S2). These results are similar to results obtained with ZIF-8, suggesting that R6G encapsulation occurred as a consequence of aperture-opening events that result from linker dissociation.[10] The surface area of UiO-66 obtained from nitrogen sorption before (947.6 m^2/g) and after aperture-opening events (948.8 m^2/g) indicated that no additional defects were generated after the encapsulation (Figure S4).[13b]

Next, similar dye encapsulation experiments were used to identify the appropriate conditions required for encapsulation of a transition metal complex and to discern the orthogonal conditions needed to suppress leaching of the guest catalyst molecules during catalysis (Figure 1a, top). R6G encapsulation was highest at elevated temperatures in polar protic solvents (e.g., methanol) and did not occur to a large extent in most polar aprotic solvents (e.g., DMF, Figure S3). Similarly, in experiments that involved exposing R6G encapsulated in UiO-66 to various solvents, dye leaching into solution was highly suppressed in aprotic solvents compared to protic solvents (See Figure S5).

Due to the linker exchange reaction occurring at the solid-liquid interface and due to the transient nature of the intermediate involved, direct observation of the proposed aperture-opened intermediate (e.g., 2, Scheme 1) would be difficult. Therefore, to further probe the mechanism for guest encapsulation, two additional experiments were carried out (Figure 1). Evidence for the existence of the aperture-opened intermediate was obtained by subjecting UiO-66 to dialysis under conditions that were best for encapsulation (Figure 1b). We hypothesized that if linkers were to dissociate from UiO-66 to form the aperture-opening intermediate, then they would diffuse through the dialysis bag instead of reassociating with UiO-66. Periodic removal of water external to the dialysis bag would ultimately result in UiO-66 that contained more missing terephthalic linkers. Consistent with these expectations, thermogravimetric analysis (TGA) revealed that the UiO-66 after dialysis in water for 18 days had less terephthalic acid linkers per zirconium node compared to UiO-66 before dialysis[13b] (Figure S6).

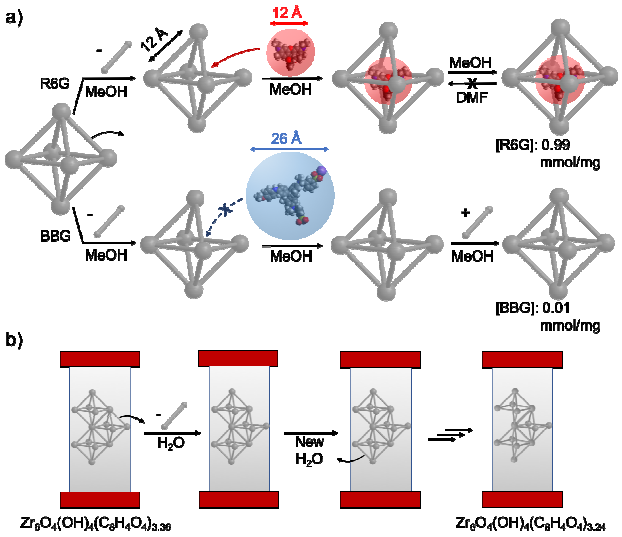


Figure 1. a) Encapsulation of R6G in UiO-66 in methanol at 55 ºC for 5 days; [Ru]@UiO-66 in DMF at 55 ºC for five days resulted in no change in [R6G]; b) Attempted encapsulation of BBG in UiO-66 in methanol at 55 ºC for five days. c)Dialysis experiment with UiO-66 in water at 55 ºC for 18 days; empirical formula for UiO-66 as determined from TGA analysis of MOF shown below corresponding dialysis bags.

Next, to illustrate that encapsulation of guest molecules requires properly-sized guest molecules for diffusion through opened apertures (e.g. 2 → 3, Scheme 1), Brilliant Blue G (BBG) was subjected to the same encapsulation conditions (Figure 1a, bot-

tom). BBG (26 Å) is larger than the successfully-encapsulated R6G (12 Å) (Figure S7 and S8), and the size of the opened apertures that would result upon dissociation of a terephthalic acid linker (12 Å). Therefore, if aperture-opening was the key step for R6G encapsulation, BBG should not be encapsulated. Consistent with this rationale and unlike R6G, BBG demonstrated no appreciable incorporation (0.01 mmol/mg) beyond the amount adsorbed to the surface of the MOF (Figure S9).

With aperture-opening in UiO-66 established as a viable synthetic method for guest encapsulation, we identified (^{tBu}PNP)Ru(CO)HCl (^{tBu}PNP = 2,6-bis((di-*tert*-butyl-phosphino)methyl)pyridine) to have the properties appropriate to demonstrate our strategy for catalysis. This complex was popularized by Milstein[14] and explored extensively by Pidko and coworkers for CO_2 hydrogenation.[12b,15] It is suitable as a guest molecule in UiO-66 because it is larger than the UiO-66 aperture size but smaller than its pore size (Figure S10). It is also appropriate for our strategy because it is soluble and stable in methanol, and it is an active catalyst for CO_2 hydrogenation in DMF/1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) mixtures.[15b] We found that the mixtures of DMF and DBU were appropriate for catalysis, because R6G dye leaching was prevented with this mixture even upon prolonged heating of the host-guest system (See Table S3).

The encapsulated catalyst, henceforth referred to as [Ru]@UiO-66, was prepared by exposing UiO-66 to (^{tBu}PNP)Ru(CO)HCl in methanol at 55 ºC for five days.[16] After a pretreatment procedure to remove surface-bound complex (See SI), the loading was determined from analysis of the digested solid by inductively coupled plasma optical emission spectrometry (ICP-OES). From the Ru to Zr ratio, the catalyst loading was determined to be 0.35 wt. ‰. The P to Ru ratio was 2.1, which suggested that the ligand did not dissociate from the ruthenium complex.[17] ^{1}H-NMR analysis of the ruthenium complex that remained in the supernatant indicated that it was unchanged during encapsulation, which further supported the absence of complex decomposition during the loading process. Powder X-ray diffraction (PXRD) analysis indicated that the crystal structure of UiO-66 was unchanged after encapsulation (Figure S11). For comparison, a sample in which the complex was adsorbed to the MOF crystals was also prepared, which will be referred to as [Ru]onUiO-66. After pretreatment of [Ru]onUiO-66, the catalyst loading was determined to be nearly an order of magnitude lower ([Ru] = 0.0375 ‰) than the loading in [Ru]@UiO-66. A size- selective poisoning study was also used to reveal that the complex was encapsulated in UiO-66 rather than adsorbed on the external surface (vide infra).

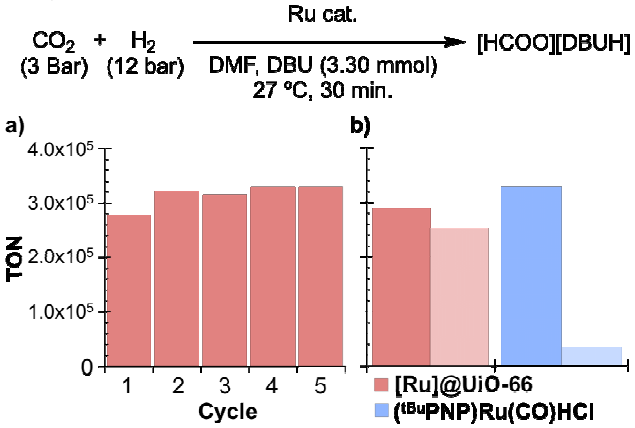


Figure 2. a) Activity of [Ru]@UiO-66 (TON = mmol $HCOO^-$/mmol Ru) upon catalyst recycling. b) comparison of catalyst activity in first cycle (dark) to that upon addition of a second aliquot of DBU (light).

Consistent with the complex integrity being maintained during the encapsulation process was the observation that [Ru]@UiO-66 is an excellent catalyst for CO_2 hydrogenation. A key difference between the homogeneous (^{tBu}PNP)Ru(CO)HCl catalyst and the [Ru]@UiO-66 encapsulated catalyst is the ability to recycle the catalyst.[18] As shown in Figure 2a, [Ru]@UiO-66 retained its activity through five cycles. PXRD analysis after the fifth cycle (See Figure S3) and the absence of terephthalic acid in the ^{1}H-NMR spectrum of the reaction supernatant provided support that the UiO-66 host maintained its integrity. The ruthenium loading in Ru@UiO-66 after the fifth cycle detected by ICP-OES was 0.35 wt. ‰ with a P:Ru ratio of 2.4, which was similar to the catalyst composition prior to the first cycle. Additionally, the supernatant from reactions using [Ru]@UiO-66 was inactive for CO_2 hydrogenation, which provides more evidence that catalyst leaching did not occur.

Recyclability and stability of the encapsulated catalyst was further evaluated by an alternative method. A second aliquot of DBU was added to reactions catalyzed by (^{tBu}PNP)Ru(CO)HCl and [Ru]@UiO-66, and the reaction mixtures were then re-subjected to the hydrogenation conditions. A significant decrease in activity was observed for the reaction catalyzed by (^{tBu}PNP)Ru(CO)HCl, whereas activity remained virtually the same for the reaction catalyzed by [Ru]@UiO-66 (Figure 2b). This outcome suggests that bimolecular decomposition lim-

its recyclability of the homogeneous catalyst, which is not the case for [Ru]@UiO-66.[15b] Additional evidence that the homogeneous catalyst undergoes bimolecular catalyst deactivation more readily than the encapsulated catalyst was obtained by evaluating the activity of the two catalysts at different catalyst concentrations (Figure S12). The homogeneous catalyst demonstrated a polynomial decrease in turnover number with increasing catalyst loading, which is characteristic of a catalyst that undergoes bimolecular catalyst deactivation. In contrast, turnover in [Ru]@UiO-66 was constant irrespective of catalyst loading, which is expected for a catalyst that does not undergo bimolecular decomposition.

To provide additional support that the ruthenium complex in [Ru]@UiO-66 is encapsulated in the MOF rather than on its surface, CO_2 hydrogenation reactions were carried out in the presence of thiols (Figure 3). Thiols are known poisons for many transition metal catalysts. As expected, when (^{tBu}PNP)Ru(CO)HCl was exposed to dodecanethiol, catalytic activity was reduced by 60%. Additionally, [Ru]onUiO-66 was poisoned by dodecanethiol to a similar degree as the homogenous catalyst. In contrast, when [Ru]@UiO-66 was exposed to dodecanethiol, catalytic activity was only reduced by 10%.

The susceptibility of the catalysts to poisoning was further probed by carrying out catalysis in the presence of a series of thiols (Figure 3). The absence of appreciable inhibition for Ru@UiO-66 in the presence of large and bulky thiols (e.g. dodecanethiol, and *tert*-butylthiol) demonstrates that the active species is encapsulated in the framework rather than bound to the surface. In all cases, catalytic activity was higher for [Ru]@UiO-66 compared to (^{tBu}PNP)Ru(CO)HCl in the presence of the thiol poisons. Moreover, all reactions catalyzed by (^{tBu}PNP)Ru(CO)HCl were poisoned to approximately the same degree regardless to the identity of the thiol poison. In contrast, poisoning in reactions catalyzed by [Ru]@UiO-66 was dependent on the identity of the thiol, with the most effective poisons being the least sterically demanding. These results are consistent with the catalyst being situated inside instead of on the surface of UiO-66 because more facile diffusion of the smaller thiols through the aperture of UiO-66 is expected, resulting in more poisoning of the catalyst than with larger and more sterically bulky thiol poisons.[19]

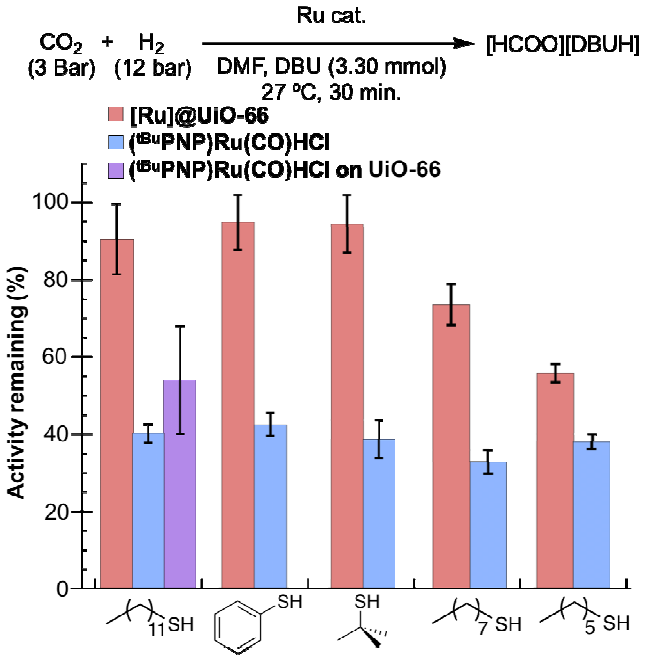


Figure 3. Comparison of the activity of homogeneous (left) and encapsulated (right) catalysts in the presence of differently sized thiol poisons.

In summary, a new method for encapsulation of a transition metal complex within a MOF was developed that capitalizes on the existence of solvent-dependent, aperture-opening events resulting from dissociative linker exchange reactions in MOFs. An encapsulated catalyst for CO_2 hydrogenation prepared using this method exhibited greater recyclability, slower bimolecular deactivation events, and resistance to poisoning compared to its homogeneous counterpart. These benefits are a direct consequence of the molecular size-selectivity and isolation of individual complexes encapsulated within the solid framework. Notably, the new method for encapsulation does not require engineering of the guest or host materials, allowing for independent modification of the host material and guest catalyst structure. This feature holds great promise to exploit the unique advantages for catalysts encapsulated in molecularly sized cages.[20] These capabilities will be pursued along with extending the aperture-opening encapsulation methodology to synthesize host-guest catalysts that will be suitable for a broader array of catalytic transformations and MOF materials.

ASSOCIATED CONTENT

Supporting Information.
Procedures and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest

ACKNOWLEDGMENT

The authors would like to thank Joseph Morabito for helpful conversations and the Trustees of Boston College for financial support. C.-K.T. acknowledges the support from NSF (CHE 1566445).

Primary Sources

Secondary Sources

Uncategorized References

(1)(a)Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724; (b)Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477.
(2)Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232.
(3)Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. *Chem. Rev.* **2012**, *112*, 1105.
(4)(a)Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450; (b)Hu, P.; Morabito, J. V.; Tsung, C.-K. *ACS Catal.* **2014**, *4*, 4409; (c)Liang, J.; Liang, Z.; Zou, R.; Zhao, Y. *Adv. Mater.* **2017**, *29*, 1701139; (d)Manna, K.; Ji, P.; Lin, Z.; Greene, F. X.; Urban, A.; Thacker, N. C.; Lin, W. *Nat. Commun.* **2016**, *7*, 12610.
(5)Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 1230444.
(6)Liao, F.-S.; Lo, W.-S.; Hsu, Y.-S.; Wu, C.-C.; Wang, S.-C.; Shieh, F.-K.; Morabito, J. V.; Chou, L.-Y.; Wu, K. C. W.; Tsung, C.-K. *J. Am. Chem. Soc.* **2017**, *139*, 6530.
(7)(a)Gadzikwa, T.; Farha, O. K.; Mulfort, K. L.; Hupp, J. T.; Nguyen, S. T. *Chem. Commun.* **2009**, 3720; (b)Baiyan Li, Y. Z., Dingxuan Ma, Tianliang Ma, Zhan Shi, Shengqian Ma *J. Am. Chem. Soc.* **2014**, *136*, 1202.
(8)(a)Jung, S.; Kim, Y.; Kim, S.-J.; Kwon, T.-H.; Huh, S.; Park, S. *Chem. Commun.* **2011**, *47*, 2904; (b)Burgess, S. A.; Kassie, A.; Baranowski, S. A.; Fritzsching, K. J.; Schmidt-Rohr, K.; Brown, C. M.; Wade, C. R. *J. Am. Chem. Soc.* **2016**, *138*, 1780; (c)Cohen, S. M.; Zhang, Z.; Boissonnault, J. A. *Inorg. Chem.* **2016**, *55*, 7281; (d)Wu, C.-D.; Lin, W. *Angew. Chem. Int. Ed.* **2007**, *46*, 1075.
(9)(a)Park, H. D.; Dincă, M.; Román-Leshkov, Y. *ACS Cent. Sci.* **2017**, *3*, 444; (b)Corma, A.; García, H.; Llabrés i Xamena, F. X. *Chem. Rev.* **2010**, *110*, 4606; (c)Caratelli, C.; Hajek, J.; Cirujano, F. G.; Waroquier, M.; Llabrés i Xamena, F. X.; Van Speybroeck, V. *J. Catal.* **2017**, *352*, 401.
(10)Morabito, J. V.; Chou, L.-Y.; Li, Z.; Manna, C. M.; Petroff, C. A.; Kyada, R. J.; Palomba, J. M.; Byers, J. A.; Tsung, C.-K. *J. Am. Chem. Soc.* **2014**, *136*, 12540.
(11)Morabito, J. V. Kinetic Methods for Understanding Linker Exchange in Metal-Organic Frameworks. Ph. D. Dissertation, Boston College, Chestnut Hill, MA, 2017.
(12)(a)Filonenko, G. A.; Conley, M. P.; Copéret, C.; Lutz, M.; Hensen, E. J. M.; Pidko, E. A. *ACS Catal.* **2013**, *3*, 2522; (b)Filonenko, G. A.; Hensen, E. J. M.; Pidko, E. A. *Catal. Sci. Technol.* **2014**, *4*, 3474; (c)Ge, H.; Jing, Y.; Yang, X. *Inorg. Chem.* **2016**, 55, 12179.
(13)(a)Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850; (b)Shearer, G. C.; Chavan, S.; Ethiraj, J.; Vitillo, J. G.; Svelle, S.; Olsbye, U.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *Chem. Mater.* **2014**, *26*, 4068; (c)Loredana Valenzano, B. C., Sachin Chavan, Silvia Bordiga, Merete H. Nilsen, Søren Jakobsen, Karl Petter Lillerud, and Carlo Lamberti *Chem. Mater.* **2011**, *23*, 17001718.
(14)Hermann, D.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. In *Organometallics*; American Chemical Society: 2002; Vol. 21, p 812.
(15)(a)Filonenko, G. A.; Smykowski, D.; Szyja, B. M.; Li, G.; Szczygieł, J.; Hensen, E. J. M.; Pidko, E. A. *ACS Catal.* **2015**, *5*, 1145; (b)Filonenko, G. A.; van Putten, R.; Schulpen, E. N.; Hensen, E. J. M.; Pidko, E. A. *ChemCatChem* **2014**, *6*, 1526.
(16)We have subsequently found that catalyst encapsulation over a 24-hour period achieved comparable loadings.
(17) We cannot rule out the possibility that a small amount of a very active heterogeneous catalyst is formed as the active species for the reaction, but control reactions revealed that if this were the case, formation of the heterogeneous catalyst would have to be templated by the homogenous complex encapsulated in the MOF (see Supporting Information).
(18)Reports that the homogeneous catalyst can be recycled have appeared previously (see ref. 14b), but these studies were conducted by cycling between hydrogenation of CO_2 and dehydrogenation of formate under base-limiting condi-tions (see SI).
(19)Dinelli, G.; Civitano, L.; Rea, M. *IEEE Transactions on Industry Applications* **1990**, *26*, 535.

(20)(a)Garcia-Garcia, P.; Muller, M.; Corma, A. *Chem. Sci.* **2014**, *5*, 2979; (b)Davis, A. V.; Raymond, K. N. *J. Am. Chem. Soc.* **2005**, *127*, 7912; (c)Hong, C. M.; Kaphan, D. M.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *J. Am. Chem. Soc.* **2017**, *139*, 8013.

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