JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by Kaohsiung Medical University

Article

Activation of Methyltrioxorhenium for Olefin Metathesis in a Zirconium-Based Metal-Organic Framework

Maciej D. Korzynski, Daniel F. Consoli, Shiran Zhang, Yuriy Roman-Leshkov, and Mircea Dinca

J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 07 May 2018

Downloaded from http://pubs.acs.org on May 7, 2018

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Activation of Methyltrioxorhenium for Olefin Metathesis in a Zirconium-Based Metal-Organic Framework

Maciej D. Korzyński,[†] Daniel F. Consoli,[‡] Shiran Zhang,[‡] Yuriy Román-Leshkov*,[‡] and Mircea Dincă*,[†]

[†] Department of Chemistry and [‡] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information Placeholder

ABSTRACT: The zirconium nodes of the metal-organic framework (MOF) known as NU-1000 serve as competent supports for the activation of methyltrioxorhenium (MTO) toward olefin metathesis. Itself inactive for olefin metathesis, MTO only becomes an active catalyst when immobilized on the strongly acidic Lewis acid sites of dehydrated NU-1000. Uptake of MTO at the dehydrated secondary building units (SBUs) occurs rapidly and quantitatively to produce a catalyst active in both gas- and liquid-phase processes. These results demonstrate for the first time the utility of MOF SBUs for olefin metathesis, an academically and industrially relevant transformation.

INTRODUCTION

Owing to their well-defined, tunable structures, metal-organic frameworks (MOFs) are gaining traction as supports for heterogeneous catalysis in large-scale processes such as olefin valorization.[1–8] Their well-defined active sites stand in contrast with the structure of metals on traditional supports such as silica, alumina, or zirconia, whose study is plagued by difficulties stemming from their lack of periodicity, the diversity of potential binding sites, and differences based on preparative method.[9–14] One prominent example of this challenge is that of heterogeneous olefin metathesis (OM) on immobilized molybdenum, tungsten, and rhenium oxide catalysts (Figure S1).[15–18] Despite decades of research, uncertainties persist regarding the intimate mechanistic details and the nature of the active species in these systems. Although MOFs have been explored for OM catalysis, it has usually been in the context of immobilizing well-defined homogeneous catalysts.[19,20] Yet, these materials are potentially excellent platforms for fundamental studies related to the large-scale industrial (i.e. oxide-based) metathesis processes: their porosity leads to a high surface area for catalyst immobilization and thus high catalyst loading, while the conserved structure across SBUs narrows the number of possibilities for active site speciation.[21–25]

The secondary building units (SBUs) are particularly relevant targets for functionalization because they can be thought of as nanoscale models of the metal oxides traditionally used as industrial catalyst supports.[26,27] Among supported OM catalysts, rhenium oxide-based systems stand out due to their activity at room temperature and their broad tolerance to a range of heterofunctionalized olefins when activated by main group alkyl species.[16,28,29] These characteristics contrast with molybdenum and tungsten systems, which are active only at significantly higher temperatures and are less tolerant of functionalized olefins. Important milestones in rhenium oxide chemistry were the discovery[30] and efficient preparation[31,32] of methyltrioxorhenium (MTO), a molecule with diverse catalytic competency.[33–37] The most salient feature of this versatile model[38–40] for immobilized rhenium oxide species in the context of heterogeneous OM catalysis is its inability to catalyze this transformation until activated on an appropriate support. The surprisingly limited scope of supports capable of triggering OM activity from MTO include alumina[41–49], silica-alumina,[41,47,50–53] niobia,[54,55] and zeolite HY.[56]

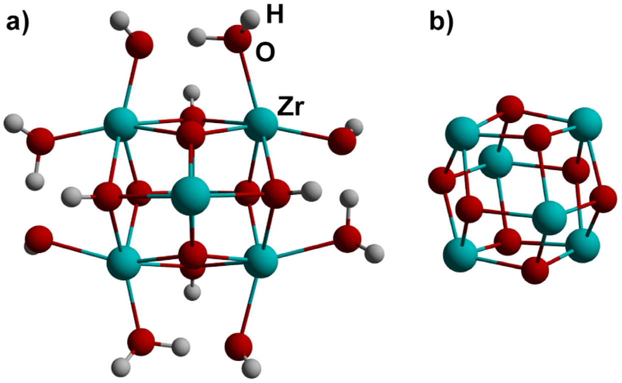

Figure 1. Idealized molecular structures of the secondary building units of a) NU-1000 and b) d-NU-1000; carboxylate groups have been omitted for clarity.

RESULTS AND DISCUSSION

In exploring OM activity with MTO, we were inspired by a recent report of MTO grafting on the zirconium SBUs (Figure 1a) of $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4](TBAPy)_2$ (NU-1000; TBAPy = 4,4′,4″,4‴-(pyrene-1,3,6,8-tetrayl)tetrakis(benzoate)).[57] In contrast to the high temperature atomic layer deposition grafting used therein, we found the autogenous vapor pressure of MTO sufficient to allow its diffusion into the pores of NU-1000 under ambient conditions. Thus, placing ground MTO crystals (1 equivalent per Zr_6 SBU) in a vial with NU-1000 leads to a slow but visible darkening of the MOF from yellow to dirty green over 48 h. Excess rhenium precursor can be removed from the resulting MTO@NU-1000 by heating to 100 °C under high vacuum ($(10^{-4}$

Torr), conditions that are sufficient for MTO sublimation. Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) analysis of digested MTO@NU-1000 showed substoichiometric rhenium incorporation (4.5±0.1 wt% as opposed to 7.8 wt% expected for a ratio of Re:Zr_6 SBU = 1:1). Powder X-ray diffraction (PXRD) analysis confirmed that MTO@NU-1000 retains its crystallinity and that no crystalline rhenium oxide is formed under these conditions (Figure S2). The material exhibits lower surface area compared to the parent material, consistent with node functionalization and a decreased pore volume (Figure S3).[58] A uniform rhenium distribution throughout the MOF particles was confirmed by scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX) mapping (Figure S4).

To probe the metathesis activity of MTO@NU-1000, we monitored the formation of ethylene and 5-decene from the homometathesis of 1-hexene: no product formation was observed even after 48 h of contact time at temperatures up to 60 °C (Figure S5). The lack of reactivity highlighted a potential difference between the Zr support in NU-1000 and the traditional silica and/or alumina supports for MTO in OM. The Lewis acidity of the support has been identified in this sense as one of the most critical factors in activating MTO.[39,43,49,52,54] Indeed, as the weakest Lewis acid, silica does not engender metathesis activity despite its ability to bind MTO.[53] Conversely, due to their more pronounced Lewis acidity, silica-alumina and alumina both activate CH_3ReO_3 for OM. The most commonly invoked interaction of Lewis acidic centers involves coordination of MTO's oxo group, which alters the precursor's electronic structure. Clearly, the presence of strong Lewis acid sites is critical for the activation of MTO towards OM.

Conveniently, the Lewis acidity of the zirconium-based MOFs can be augmented in a facile manner through high-temperature dehydration of the SBU.[27,59,60] In the case of NU-1000, the loss of eight water molecules from $[Zr_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(OH)_4(H_2O)_4]^{8+}$ leads to completely aprotic $[Zr_6(\mu_3\text{-O})_8]^{8+}$ nodes (Figure 1b).[61–63] These exhibit four Zr^{4+} ions that are bound, on average, to two fewer oxygen atoms and are thus more acidic than those in the original SBU. We surmised that the dehydrated material (d-NU-1000) would be a more active support for MTO both because of the increased Lewis acidity and because the absence of protons near the presumed active site would prevent undesired protonation of Re-alkylidene species.[64,65]

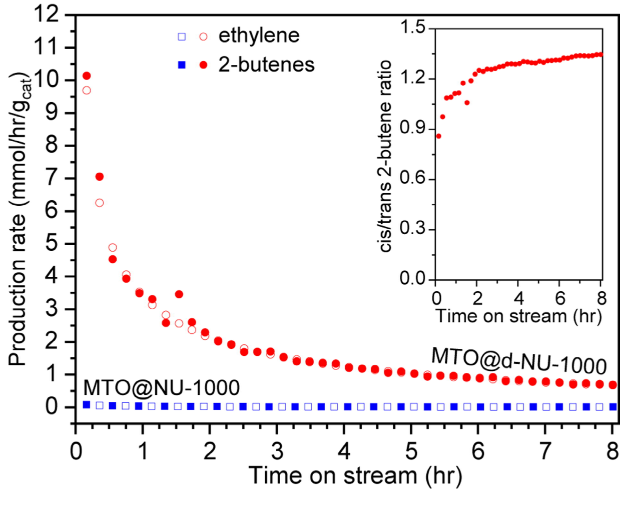

Figure 2. Propylene metathesis activity of MTO@d-NU-1000

Promisingly, uptake of 0.5 equivalents of MTO into d-NU-1000 was rapid and quantitative, giving a Re mass loading of 4.4±0.2 wt%, in good agreement with 4.2 wt% expected for the uptake of 0.5 Re per Zr_6 cluster in MTO@d-NU-1000. Moreover, heating MTO@d-NU-1000 did not release any MTO, confirming that all rhenium precursor is grafted onto the MOF support. As before, crystallinity is retained and no rhenium oxide formation is observed by PXRD analysis of MTO@d-NU-1000 (Figure S6), which otherwise shows homogeneous distribution of Re as judged from the SEM-EDX mapping (Figure S8). Most notably, and clearly indicative of its increased reactivity, brown MTO@d-NU-1000 is air-sensitive and discolors to yellow, the color of the parent d-NU-1000 upon exposure to air (Figure S10). This contrasts with the behavior of MTO@NU-1000, which is not air-sensitive and is inactive for OM, as discussed above.

Initial confirmation of OM activity with MTO@d-NU-1000 came from the 1-hexene test reaction: ^1H NMR spectroscopy of a reaction mixture in benzene-d_6 showed new resonances at 5.45 ppm and 5.25 ppm, indicating the formation of 5-decene and ethylene, respectively (Figure S12). Although the isomerization of terminal olefins is an undesired side-reaction on strongly acidic supports and can lead to costly and energy-intensive separations,[51,53,56] we did not observe any other internal olefins other than 5-decene, the desired product (Figure S13). This suggests a moderate Lewis acidity and the absence of Brønsted acidic sites in d-NU-1000, which provides a middle ground between successful MTO activation and deleterious olefin isomerization. Control experiments showed that non-grafted d-NU-1000 is not competent for 1-hexene metathesis reactivity even at 60 °C (Figure S11). Finally, PXRD analysis of the spent catalyst confirmed retention of crystallinity during catalysis (Figure S18).

Encouraged by these results, we sought to address a more relevant reaction in industrial OM catalysis: the on-purpose formation of propylene by cross-metathesis of ethylene with 2-butenes.[66,67] The reverse reaction, propylene homometathesis to ethylene and 2-butene, is a good proxy for evaluating catalytic activity in this transformation. It was thus used as an initial probe of gas-phase catalytic activity with MTO@d-NU-1000. At room temperature, the catalyst mediates propylene metathesis with an initial TOF of 86 hr^{-1} after 10 min and a decaying rate profile typical of MTO-derived systems (Figures 2 and S15).[45] Our system is less active than reported MTO immobilized on alumina, which exhibits TOF of 2700 hr^{-1} after 6 min under similar conditions. This difference in reactivity also applies to MTO/SiO_2-Al_2O_3, which has been shown to be ten times more active than MTO/γ-Al_2O_3 in batch experiments.[49] However, it is important to note that this comparison involves supports based on different Lewis acidic centers. To the best of our knowledge no study on OM activity of MTO on ZrO_2 has been published. In addition to the previously mentioned MTO deposited on silica, TiO_2[200] is also catalytically incompetent in the activation of MTO for OM.[54]

The steady-state ratio of cis- to trans-2-butene was approximately 1.3 (Figure 2, inset); the slight preference for the less thermodynamically stable product is in line with previous reports of supported MTO catalysts and is due to the sterically crowded profile of such species.[45] No 1-butene formation was detected by gas chromatography, paralleling the lack of isomerization observed with liquid phase experiments (Figure S17). Importantly, MTO@d-NU-1000 remains active and displays 182 turnover numbers after 20 hours (Figure S16). Mirroring the liquid phase experiments, the spent MOF remains crystalline and porous, as evidenced by PXRD and BET analysis (Figures S18 and S19). In line with earlier experiments, NU-1000 and MTO@NU-1000 were essentially inactive for propylene metathesis under identical conditions (Figures 2 and S14).

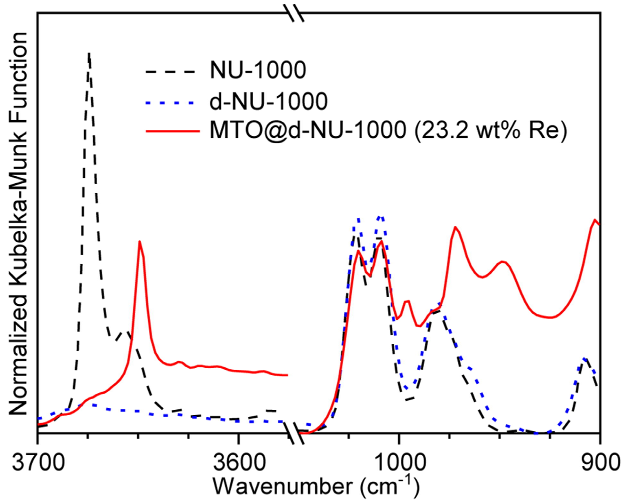

Figure 3. Partial DRIFTS spectrum of MTO@d-NU-1000

To gain information on the nature of Re species responsible for catalysis, we grafted a higher loading of MTO into d-NU-1000 to increase the spectroscopic features observable by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Notably, the Re uptake remains quantitative up to at least 23.2±0.7 wt%, which corresponds to approximately 3.6 Re equivalents per SBU (for characterization see Figures S6, S7 and S9). DRIFTS analysis of this more highly grafted MTO@d-NU-1000 revealed bands at 995, 971, and 948 cm^{-1} that are typically ascribed to the symmetric and two asymmetric Re=O stretches, respectively (Figure 3).[68] Lifting of the asymmetric stretch degeneracy points to a symmetry lower than the idealized C_{3v} symmetry of MTO and is suggestive of rigidly immobilized species.[69] Even though C–H stretches from MTO are often diagnostic of the nature of the immobilized species, the parent MOF obscures the relevant 2800-3200 cm^{-1} region in our system (Figure S20). However, MTO@d-NU-1000 does display a sharp band at 3649 cm^{-1} that is absent in d-NU-1000. It is known that pure MTO exhibits a weak combination band at 3637 cm^{-1} originating from much more intense fundamental modes at 740 cm^{-1} and 2900 cm^{-1} (Figure S21).[70] However, based on the intensity of the signal at 3649 cm^{-1} observed in MTO@d-NU-1000, it is unlikely that this band originates from MTO vibrational modes, given that the fundamentals giving rise to this mode are not visible. Instead, based on comparisons with the spectrum of activated NU-1000, we tentatively ascribe the sharp signal at 3649 cm^{-1} to a bridging O-H group. To validate this hypothesis, we prepared and deposited deuterated MTO (Figure S23) to investigate the expected isotopic shift associated with the formation of O-D moieties. Indeed, the most pronounced change in the DRIFTS spectrum of MTO-*d3*@d-NU-1000 compared with the non-deuterated material is the disappearance of the band at 3649 cm^{-1} and the appearance of a qualitatively similar band at 2691 cm^{-1} (Figure S24). The latter agrees well with the theoretical shift calculated using the harmonic oscillator approximation (2657 cm^{-1}). An additional weak band at 2109 cm^{-1} is in the region expected for C-D stretches. Extensive studies on MTO immobilized on alumina have shown that the active site is formed by C-H bond scission to yield a bridging methylene species with one of the oxygen atoms acting as an acceptor of a proton.[42] We expect that the node of d-NU-1000 could also facilitate such proton migration (Figure S25), which would explain the reappearance of the O-H stretch in the spectrum. However, the previous studies on MTO interaction with heterogeneous supports suggests that more than one way of interaction might be operational.

CONCLUSION

In summary, although MTO binds to NU-1000 both before and after node dehydration, only the dehydrated MOF produces an active olefin metathesis catalyst. This markedly different reactivity is a testament to the significant difference in the Lewis acidity of the Zr^{4+}-based SBUs before and after dehydration. This reactivity trend is in agreement with the observed increasing Lewis acidity trend in transitioning from silica to silica-alumina and alumina. The results herein demonstrate for the first time that MOF SBUs can enable catalytic olefin metathesis. In this context, d-NU-1000 joins a select group of heterogeneous supports capable of activating MTO for this reaction. With OM activity thus established, future efforts in our lab will follow documented approaches for mechanistic investigations at MOF nodes[71–73] to elucidate the precise nature of the Re active site in this system.

ASSOCIATED CONTENT

Supporting Information

Experimental details, PXRD patterns, nitrogen isotherms, SEM-EDX maps, additional DRIFTS spectra, sample ^1H NMR spectra and GC traces, site time yield and TOF plots as well as the graphical representation of the plausible MTO binding mode are available in the supporting information pdf file.

AUTHOR INFORMATION

Corresponding Authors

E-mail: mdinca@mit.edu
E-mail: yroman@mit.edu

ORCID

Maciej D. Korzyński: 0000-0002-6577-1821
Daniel F. Consoli: 0000-0002-1061-3391
Yuriy Román-Leshkov: 0000-0002-0025-4233
Mircea Dincă: 0000-0002-1262-1264

Notes

The authors declare no competing financial interests. MDK and DFC contributed equally.

ACKNOWLEDGMENT

This research was supported through a Research Agreement with Saudi Aramco, a Founding Member of the MIT Energy Initiative. The authors thank Prof. Chao Wang for his advice regarding the preparation of alkyltin reagents, Dr. Robert Day for collection of the SEM-EDX data and Mr. Wesley Transue for useful discussions.

REFERENCES

(1) Cho, S.-H.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. A Metal–organic Framework Material That Functions as an Enantioselective Catalyst for Olefin Epoxidation. *Chem. Commun.* **2006**, No. 24, 2563–2565.
(2) Song, F.; Wang, C.; Falkowski, J. M.; Ma, L.; Lin, W. Isoreticular Chiral Metal-Organic Frameworks for Asymmetric Alkene Epoxidation: Tuning Catalytic Activity by Controlling Framework Catenation and Varying Open Channel Sizes. *J. Am. Chem. Soc.* **2010**, *132* (43), 15390–15398.
(3) Zhang, J.; Biradar, A. V.; Pramanik, S.; Emge, T. J.; Asefa, T.; Li, J. A New Layered Metal–organic Framework as a Promising

Heterogeneous Catalyst for Olefin Epoxidation Reactions. *Chem. Commun.* **2012**, *48* (52), 6541–6543.

(4) Mlinar, A. N.; Keitz, B. K.; Gygi, D.; Bloch, E. D.; Long, J. R.; Bell, A. T. Selective Propene Oligomerization with Nickel(II)-Based Metal–Organic Frameworks. *ACS Catal.* **2014**, *4* (3), 717–721.

(5) Metzger, E. D.; Brozek, C. K.; Comito, R. J.; Dincă, M. Selective Dimerization of Ethylene to 1-Butene with a Porous Catalyst. *ACS Cent. Sci.* **2016**, *2* (3), 148–153.

(6) Comito, R. J.; Fritzsching, K. J.; Sundell, B. J.; Schmidt-Rohr, K.; Dincă, M. Single-Site Heterogeneous Catalysts for Olefin Polymerization Enabled by Cation Exchange in a Metal-Organic Framework. *J. Am. Chem. Soc.* **2016**, *138* (32), 10232–10237.

(7) Li, Z.; Peters, A. W.; Bernales, V.; Ortuño, M. A.; Schweitzer, N. M.; DeStefano, M. R.; Gallington, L. C.; Platero-Prats, A. E.; Chapman, K. W.; Cramer, C. J.; Gagliardi, L.; Hupp, J. T.; Farha, O. K. Metal–Organic Framework Supported Cobalt Catalysts for the Oxidative Dehydrogenation of Propane at Low Temperature. *ACS Cent. Sci.* **2017**, *3* (1), 31–38.

(8) Bernales, V.; Yang, D.; Yu, J.; Gümüşlü, G.; Cramer, C. J.; Gates, B. C.; Gagliardi, L. Molecular Rhodium Complexes Supported on the Metal-Oxide-Like Nodes of Metal Organic Frameworks and on Zeolite HY: Catalysts for Ethylene Hydrogenation and Dimerization. *ACS Appl. Mater. Interfaces* **2017**, *9* (39), 33511–33520.

(9) Ma, Z.; Zaera, F. Heterogeneous Catalysis by Metals. In *Encyclopedia of Inorganic Chemistry*; John Wiley & Sons, Ltd: Chichester, UK, 2006; Vol. 30, pp 27–38.

(10) Breysse, M.; Afanasiev, P.; Geantet, C.; Vrinat, M. Overview of Support Effects in Hydrotreating Catalysts. *Catal. Today* **2003**, *86* (1–4), 5–16.

(11) Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. Use of DFT to Achieve a Rational Understanding of Acid-Basic Properties of γ-Alumina Surfaces. *J. Catal.* **2004**, *226* (1), 54–68.

(12) Joubert, J.; Delbecq, F.; Sautet, P.; Le Roux, E.; Taoufik, M.; Thieuleux, C.; Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Basset, J. M. Molecular Understanding of Alumina Supported Single-Site Catalysts by a Combination of Experiment and Theory. *J. Am. Chem. Soc.* **2006**, *128* (28), 9157–9169.

(13) Gao, F.; Goodman, D. W. Model Catalysts: Simulating the Complexities of Heterogeneous Catalysts. *Annu. Rev. Phys. Chem.* **2012**, *63* (1), 265–286.

(14) Gates, B. C.; Flytzani-Stephanopoulos, M.; Dixon, D. A.; Katz, A. Atomically Dispersed Supported Metal Catalysts: Perspectives and Suggestions for Future Research. *Catal. Sci. Technol.* **2017**, *7* (19), 4259–4275.

(15) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*, 2 edition.; Academic Press, 1997.

(16) Lwin, S.; Wachs, I. E. Olefin Metathesis by Supported Metal Oxide Catalysts. *ACS Catal.* **2014**, *4* (8), 2505–2520.

(17) Gholampour, N.; Yusubov, M.; Verpoort, F. Investigation of the Preparation and Catalytic Activity of Supported Mo, W, and Re Oxides as Heterogeneous Catalysts in Olefin Metathesis. *Catal. Rev.* **2016**, *58* (1), 113–156.

(18) Copéret, C.; Comas-Vives, A.; Conley, M. P.; Estes, D. P.; Fedorov, A.; Mougel, V.; Nagae, H.; Núñez-Zarur, F.; Zhizhko, P. A. Surface Organometallic and Coordination Chemistry toward Single-Site Heterogeneous Catalysts: Strategies, Methods, Structures, and Activities. *Chem. Rev.* **2016**, *116* (2), 323–421.

(19) Chołuj, A.; Zieliński, A.; Grela, K.; Chmielewski, M. J. Metathesis@MOF: Simple and Robust Immobilization of Olefin Metathesis Catalysts inside (Al)MIL-101-NH_2. *ACS Catal.* **2016**, *6* (10), 6343–6349.

(20) Yuan, J.; Fracaroli, A. M.; Klemperer, W. G. Convergent Synthesis of a Metal–Organic Framework Supported Olefin Metathesis Catalyst. *Organometallics* **2016**, *35* (12), 2149–2155.

(21) Yoon, M.; Srirambalaji, R.; Kim, K. Homochiral Metal–Organic Frameworks for Asymmetric Heterogeneous Catalysis. *Chem. Rev.* **2012**, *112* (2), 1196–1231.

(22) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X. Metal Organic Framework Catalysis: Quo Vadis ? *ACS Catal.* **2014**, *4* (2), 361–378.

(23) Cohen, S. M.; Zhang, Z.; Boissonnault, J. A. Toward “metalloMOFzymes”: Metal–Organic Frameworks with Single-Site Metal Catalysts for Small-Molecule Transformations. *Inorg. Chem.* **2016**, *55* (15), 7281–7290.

(24) Xu, W.; Thapa, K. B.; Ju, Q.; Fang, Z.; Huang, W. Heterogeneous Catalysts Based on Mesoporous Metal–organic Frameworks. *Coord. Chem. Rev.* **2017,** doi: 10.1016/j.ccr.2017.10.014.

(25) Rogge, S. M. J.; Bavykina, A.; Hajek, J.; Garcia, H.; Olivos-Suarez, A. I.; Sepúlveda-Escribano, A.; Vimont, A.; Clet, G.; Bazin, P.; Kapteijn, F.; Daturi, M.; Ramos-Fernandez, E. V.; Llabrés i Xamena, F. X.; Van Speybroeck, V.; Gascon, J. Metal–organic and Covalent Organic Frameworks as Single-Site Catalysts. *Chem. Soc. Rev.* **2017**, *46* (11), 3134–3184.

(26) Platero-Prats, A. E.; Mavrandonakis, A.; Gallington, L. C.; Liu, Y.; Hupp, J. T.; Farha, O. K.; Cramer, C. J.; Chapman, K. W. Structural Transitions of the Metal-Oxide Nodes within Metal–Organic Frameworks: On the Local Structures of NU-1000 and UiO-66. *J. Am. Chem. Soc.* **2016**, *138* (12), 4178–4185.

(27) Rimoldi, M.; Howarth, A. J.; DeStefano, M. R.; Lin, L.; Goswami, S.; Li, P.; Hupp, J. T.; Farha, O. K. Catalytic Zirconium/Hafnium-Based Metal–Organic Frameworks. *ACS Catal.* **2017**, *7* (2), 997–1014.

(28) Mol, J. C. Olefin Metathesis over Supported Rhenium Oxide Catalysts. *Catal. Today* **1999**, *51* (2), 289–299.

(29) Moses, A. W.; Leifeste, H. D.; Ramsahye, N. A.; Eckert, J.; Scott, S. L. Supported Re Catalysts for Metathesis of Functionalized Olefins. In *Catalysis of Organic Reactions*; Schmidt, S. R., Ed.; CRC Press: Boca Raton, 2007; pp 13–22.

(30) Beattie, I. R.; Jones, P. J. Methyltrioxorhenium. An Air-Stable Compound Containing a Carbon-Rhenium Bond. *Inorg. Chem.* **1979**, *18* (8), 2318–2319.

(31) Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. Methylrhenium Oxides: Synthesis from R_2O_7 and Catalytic Activity in Olefin Metathesis. *Angew. Chemie Int. Ed. English* **1988**, *27* (3), 394–396.

(32) Tosh, E.; Mitterpleininger, J. K. M.; Rost, A. M. J.; Veljanovski, D.; Herrmann, W. A.; Kühn, F. E. Methyltrioxorhenium Revisited: Improving the Synthesis for a Versatile Catalyst. *Green Chem.* **2007**, *9* (12), 1296.

(33) Romão, C. C.; Kühn, F. E.; Herrmann, W. A. Rhenium(VII) Oxo and Imido Complexes: Synthesis, Structures, and Applications. *Chem. Rev.* **1997**, *97* (8), 3197–3246.

(34) Herrmann, W. A.; Kühn, F. E. Organorhenium Oxides †. *Acc. Chem. Res.* **1997**, *30* (4), 169–180.

(35) Kühn, F. E.; Scherbaum, A.; Herrmann, W. A. Methyltrioxorhenium and Its Applications in Olefin Oxidation, Metathesis and Aldehyde Olefination. *J. Organomet. Chem.* **2004**, *689* (24), 4149–4164.

(36) Jain, K. R.; Kühn, F. E. Immobilization of organorhenium(VII) Oxides. *J. Organomet. Chem.* **2007**, *692* (25), 5532–5540.

(37) Hudson, A.; Betz, D.; Kühn, F. E.; Jiménez-Alemán, G. H.; Boland, W. Methyltrioxorhenium. In *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, Ltd: Chichester, UK, 2013; Vol. 1, pp 1–11.

(38) Copéret, C. Design and Understanding of Heterogeneous Alkene Metathesis Catalysts. *Dalt. Trans.* **2007**, No. 47, 5498.

(39) Lai, Y.-Y.; Bornand, M.; Chen, P. Homogeneous Model Complexes for Supported Rhenia Metathesis Catalysts. *Organometallics* **2012**, *31* (21), 7558–7565.

(40) Valla, M.; Conley, M. P.; Copéret, C. $MeReO_3/Al_2O_3$ and Me_4Sn-Activated Re_2O_7/Al_2O_3 Alkene Metathesis Catalysts Have Similar Active Sites. *Catal. Sci. Technol.* **2015**, *5* (3), 1438–1442.

(41) Rost, A. M. J.; Schneider, H.; Zoller, J. P.; Herrmann, W. A.; Kühn, F. E. Methyltrioxorhenium Heterogenized on Commercially Available Supporting Materials as Cyclooctene Metathesis Catalyst. *J. Organomet. Chem.* **2005**, *690* (21–22), 4712–4718.

(42) Salameh, A.; Joubert, J.; Baudouin, A.; Lukens, W.; Delbecq, F.; Sautet, P.; Basset, J. M.; Copéret, C. CH_3ReO_3 on γ-Al_2O_3: Understanding Its Structure, Initiation, and Reactivity in Olefin Metathesis. *Angew. Chemie Int. Ed.* **2007**, *46* (21), 3870–3873.

(43) Oikawa, T.; Masui, Y.; Tanaka, T.; Chujo, Y.; Onaka, M. Lewis Acid-Modified Mesoporous Alumina: A New Catalyst Carrier

for Methyltrioxorhenium in Metathesis of Olefins Bearing Functional Groups. *J. Organomet. Chem.* **2007**, *692* (1–3), 554–561.

(44) Salameh, A.; Baudouin, A.; Basset, J.-M.; Copéret, C. Tuning the Selectivity of Alumina-Supported $(CH_3)ReO_3$ by Modifying the Surface Properties of the Support. *Angew. Chemie Int. Ed.* **2008**, *47* (11), 2117–2120.

(45) Salameh, A.; Baudouin, A.; Soulivong, D.; Boehm, V.; Roeper, M.; Basset, J.-M.; Copéret, C. CH_3-ReO_3 on γ-Al_2O_3: Activity, Selectivity, Active Site and Deactivation in Olefin Metathesis. *J. Catal.* **2008**, *253* (1), 180–190.

(46) Wischert, R.; Copéret, C.; Delbecq, F.; Sautet, P. Revisiting the Structure of Methyltrioxorhenium Chemisorbed on Alumina. *ChemCatChem* **2010**, *2* (7), 812–815.

(47) Stekrova, M.; Zdenkova, R.; Vesely, M.; Vyskocilova, E.; Cerveny, L. Immobilization of Methyltrioxorhenium on Mesoporous Aluminosilicate Materials. *Materials (Basel).* **2014**, *7* (12), 2650–2668.

(48) Valla, M.; Wischert, R.; Comas-Vives, A.; Conley, M. P.; Verel, R.; Copéret, C.; Sautet, P. Role of Tricoordinate Al Sites in CH_3ReO_3/Al_2O_3 Olefin Metathesis Catalysts. *J. Am. Chem. Soc.* **2016**, *138* (21), 6774–6785.

(49) Gallo, A.; Fong, A.; Szeto, K. C.; Rieb, J.; Delevoye, L.; Gauvin, R. M.; Taoufik, M.; Peters, B.; Scott, S. L. Ligand Exchange-Mediated Activation and Stabilization of a Re-Based Olefin Metathesis Catalyst by Chlorinated Alumina. *J. Am. Chem. Soc.* **2016**, *138* (39), 12935–12947.

(50) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. Methyltrioxorhenium as Catalyst for Olefin Metathesis. *Angew. Chemie Int. Ed. English* **1991**, *30* (12), 1636–1638.

(51) Mathew, T. M.; du Plessis, J. A. K.; Prinsloo, J. J. Methyltrioxorhenium on Silica–alumina as Metathesis Catalyst of 1-Octene. *J. Mol. Catal. A Chem.* **1999**, *148* (1–2), 157–164.

(52) Moses, A. W.; Ramsahye, N. A.; Raab, C.; Leifeste, H. D.; Chattopadhyay, S.; Chmelka, B. F.; Eckert, J.; Scott, S. L. Methyltrioxorhenium Interactions with Lewis Acid Sites of an Amorphous Silica−Alumina. *Organometallics* **2006**, *25* (9), 2157–2165.

(53) Moses, A. W.; Raab, C.; Nelson, R. C.; Leifeste, H. D.; Ramsahye, N. A.; Chattopadhyay, S.; Eckert, J.; Chmelka, B. F.; Scott, S. L. Spectroscopically Distinct Sites Present in Methyltrioxorhenium Grafted onto Silica−Alumina, and Their Abilities to Initiate Olefin Metathesis. *J. Am. Chem. Soc.* **2007**, *129* (28), 8912–8920.

(54) Buffon, R.; Auroux, A.; Lefebvre, F.; Leconte, M.; Choplin, A.; Basset, J.-M.; Herrmann, W. A. A Surface Organometallic Approach to the Synthesis of Rhenium-Based Catalysts for the Metathesis of Olefins: CH_3ReO_3/Nb_2O_5. *J. Mol. Catal.* **1992**, *76* (1–3), 287–295.

(55) Buffon, R.; Choplin, A.; Leconte, M.; Basset, J.-M.; Touroude, R.; Herrmann, W. A. Surface Organometallic Chemistry of Rhenium: Attempts to Characterize a Surface Carbene in Metathesis of Olefins with the Catalyst CH_3ReO_3/Nb_2O_5. *J. Mol. Catal.* **1992**, *72* (2), L7–L10.

(56) Bein, T.; Huber, C.; Moller, K.; Wu, C.-G.; Xu, L. Methyltrioxorhenium Encapsulated in Zeolite Y: Tunable Olefin Metathesis Catalyst. *Chem. Mater.* **1997**, *9* (11), 2252–2254.

(57) Rimoldi, M.; Hupp, J. T.; Farha, O. K. Atomic Layer Deposition of Rhenium–Aluminum Oxide Thin Films and ReO_x Incorporation in a Metal–Organic Framework. *ACS Appl. Mater. Interfaces* **2017**, *9* (40), 35067–35074.

(58) Drout, R. J.; Otake, K.; Howarth, A. J.; Islamoglu, T.; Zhu, L.; Xiao, C.; Wang, S.; Farha, O. K. Efficient Capture of Perrhenate and Pertechnetate by a Mesoporous Zr Metal–Organic Framework and Examination of Anion Binding Motifs. *Chem. Mater.* **2018**, *30* (4), 1277–1284.

(59) Valenzano, L.; Civalleri, B.; Chavan, S.; Bordiga, S.; Nilsen, M. H.; Jakobsen, S.; Lillerud, K. P.; Lamberti, C. Disclosing the Complex Structure of UiO-66 Metal Organic Framework: A Synergic Combination of Experiment and Theory. *Chem. Mater.* **2011**, *23* (7), 1700–1718.

(60) Taddei, M. When Defects Turn into Virtues: The Curious Case of Zirconium-Based Metal-Organic Frameworks. *Coord. Chem. Rev.* **2017**, *343*, 1–24.

(61) Planas, N.; Mondloch, J. E.; Tussupbayev, S.; Borycz, J.; Gagliardi, L.; Hupp, J. T.; Farha, O. K.; Cramer, C. J. Defining the Proton Topology of the Zr_6-Based Metal–Organic Framework NU-1000. *J. Phys. Chem. Lett.* **2014**, *5* (21), 3716–3723.

(62) Mondloch, J. E.; Katz, M. J.; Isley III, W. C.; Ghosh, P.; Liao, P.; Bury, W.; Wagner, G. W.; Hall, M. G.; DeCoste, J. B.; Peterson, G. W.; Snurr, R. Q.; Cramer, C. J.; Hupp, J. T.; Farha, O. K. Destruction of Chemical Warfare Agents Using Metal–organic Frameworks. *Nat. Mater.* **2015**, *14* (5), 512–516.

(63) Kim, I. S.; Borycz, J.; Platero-Prats, A. E.; Tussupbayev, S.; Wang, T. C.; Farha, O. K.; Hupp, J. T.; Gagliardi, L.; Chapman, K. W.; Cramer, C. J.; Martinson, A. B. F. Targeted Single-Site MOF Node Modification: Trivalent Metal Loading via Atomic Layer Deposition. *Chem. Mater.* **2015**, *27* (13), 4772–4778.

(64) LaPointe, A. M.; Schrock, R. R. Alkyl, Alkylidene, and Alkylidyne Complexes of Rhenium. *Organometallics* **1995**, *14*, 1875–1884.

(65) Chabanas, M.; Baudouin, A.; Copéret, C.; Basset, J.-M.; Lukens, W.; Lesage, A.; Hediger, S.; Emsley, L. Perhydrocarbyl Re VII Complexes: Comparison of Molecular and Surface Complexes. *J. Am. Chem. Soc.* **2003**, *125* (2), 492–504.

(66) Plotkin, J. S. The Propylene Quandary https://www.acs.org/content/acs/en/pressroom/cutting-edge-chemistry/the-propylene-quandary.html (accessed Jan 2, 2018).

(67) Mol, J. C. Industrial Applications of Olefin Metathesis. *J. Mol. Catal. A Chem.* **2004**, *213* (1), 39–45.

(68) Vaz, P. D.; Ribeiro-Claro, P. J. A. The Role of C-H···O Interactions in the Solid and Liquid-Phase Structures of Methyltrioxo Rhenium. *Eur. J. Inorg. Chem.* **2005**, 1836–1840.

(69) Parker, S. F.; Herman, H. The Vibrational Spectrum of methyltrioxorhenium(VII). *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2000**, *56* (6), 1123–1129.

(70) Mink, J.; Keresztury, G.; Stirling, A.; Herrmann, W. A. Vibrational Spectroscopic and Force Field Studies of organorhenium(VII) Trioxides-I. Methyltrioxorhenium(VII), ethyltrioxorhenium(VII) and (N-propyl)trioxorhenium(VII). *Spectrochim. Acta Part A Mol. Spectrosc.* **1994**, *50* (12), 2039–2057.

(71) Metzger, E. D.; Comito, R. J.; Hendon, C. H.; Dincă, M. Mechanism of Single-Site Molecule-Like Catalytic Ethylene Dimerization in Ni-MFU-4l. *J. Am. Chem. Soc.* **2017**, *139* (2), 757–762.

(72) Comito, R. J.; Metzger, E. D.; Wu, Z.; Zhang, G.; Hendon, C. H.; Miller, J. T.; Dincă, M. Selective Dimerization of Propylene with Ni-MFU-4l. *Organometallics* **2017**, *36* (9), 1681–1683.

(73) Dubey, R. J. C.; Comito, R. J.; Wu, Z.; Zhang, G.; Rieth, A. J.; Hendon, C. H.; Miller, J. T.; Dincă, M. Highly Stereoselective Heterogeneous Diene Polymerization by Co-MFU-4l : A Single-Site Catalyst Prepared by Cation Exchange. *J. Am. Chem. Soc.* **2017**, *139* (36), 12664–12669.

Insert Table of Contents artwork here