

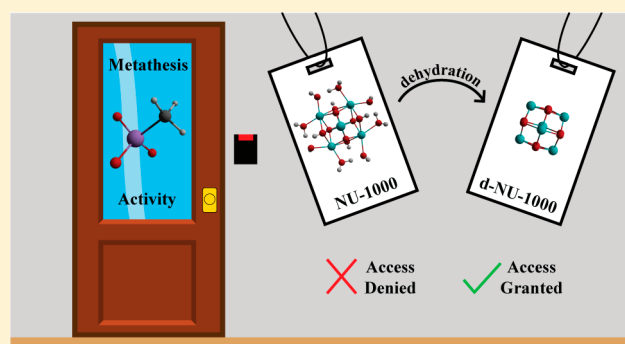
Activation of Methyltrioxorhenium for Olefin Metathesis in a Zirconium-Based Metal–Organic Framework

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Supporting Information

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 becomes an active catalyst only 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 discovery³⁰ 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

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 $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_4(\text{H}_2\text{O})_4](\text{TBAPy})_2$ (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 equiv 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

Received: March 13, 2018

Published: May 7, 2018

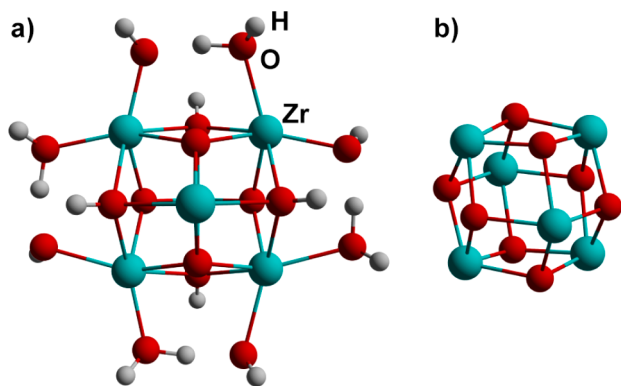


Figure 1. Idealized molecular structures of the secondary building units of (a) NU-1000 and (b) d-NU-1000. Carboxylate groups have been omitted for clarity.

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:Zr₆ 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@d-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 CH₃ReO₃ 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 toward 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 [Zr₆(μ₃-O)₄(μ₃-OH)₄(OH)₄(H₂O)₄]⁸⁺ leads to completely aprotic [Zr₆(μ₃-O)₈]⁸⁺ nodes (Figure 1b).^{61–63} These exhibit four Zr⁴⁺ 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}

Promisingly, uptake of 0.5 equiv 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 Zr₆ 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 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 nongrafted 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).

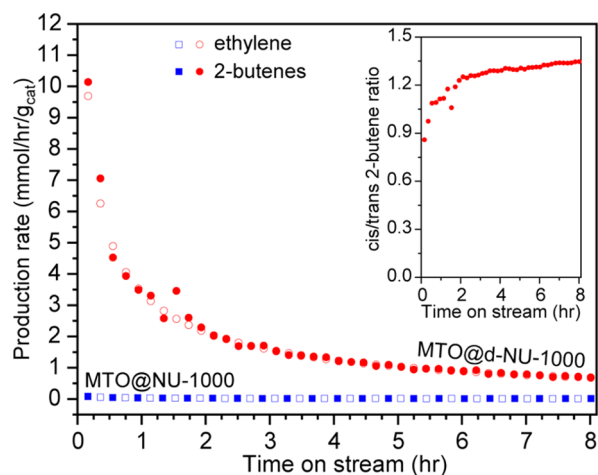


Figure 2. Propylene metathesis activity of MTO@d-NU-1000.

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 turnover frequency (TOF) of 86 h⁻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 a TOF of 2700 h⁻¹ after 6 min under similar conditions. This difference in reactivity also applies to MTO/SiO₂–Al₂O₃, which has been shown to be 10

times more active than MTO/ γ -Al₂O₃ 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 ZrO₂ has been published. In addition to the previously mentioned MTO deposited on silica, TiO₂[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 turnovers after 20 h (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).

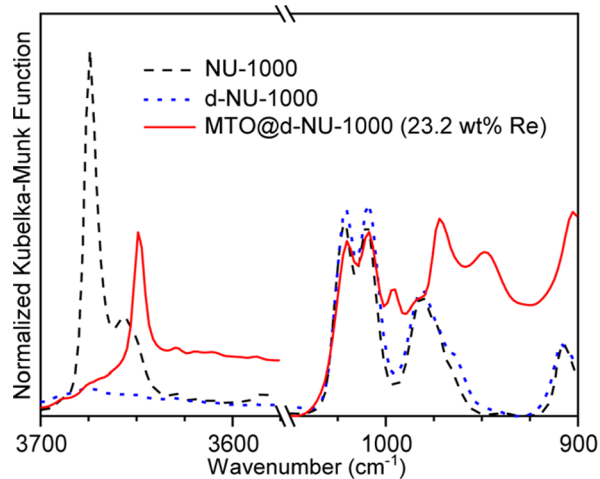


Figure 3. Partial DRIFTS spectrum of MTO@d-NU-1000.

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 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 nondeuterated 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 suggest 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 Zr⁴⁺-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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b02837.

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 (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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.

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