



CORNELL UNIVERSITY LIBRARY

Subscriber access provided by CORNELL UNIVERSITY LIBRARY

Article

Extension of the Surface Organometallic Chemistry to Metal-Organic Framework: development of well-defined single site [(#Zr-O-)W(=O)(CH2tBu)3] olefin metathesis catalyst.

Zeynabou Thiam, Edy Abou-Hamad, Busra Dereli, Lingmei Liu, Abdul-Hamid Emwas, Rafia Ahmad, Hao Jiang, Abdulrahman Adamu Isah, Papa Birame Ndiaye, Mostafa Taoufik, Yu Han, Luigi Cavallo, Jean-Marie Basset, and Mohamed Eddaoudi

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.0c06925 • Publication Date (Web): 09 Sep 2020 Downloaded from pubs.acs.org on September 9, 2020

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.

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.

Extension of the Surface Organometallic Chemistry to Metal-Organic Framework: development of well-defined single site $[(\equiv Zr-O-)W(=O)(CH_2^tBu)_3]$ olefin metathesis catalyst.

Zeynabou Thiam^{1, 2, 3}, Edy Abou-Hamad⁴, Busra Dereli³, Lingmei Liu¹, Abdul-Hamid Emwas⁴, Rafia Ahmad³, Hao Jiang^{1,2}, Abdulrahman Adamu Isah⁵, Papa Birame Ndiaye⁶, Mostafa Taoufik⁵, Yu Han¹, Luigi Cavallo³, Jean-Marie Basset^{3, *}, Mohamed Eddaoudi^{1, 2, *}.

¹ Advanced Membranes and Porous Materials Center (AMPMC), Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia.

²Functional Materials Design, Discovery & Development Research Group (FMD3)

³ KAUST Catalysis Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

⁴King Abdullah University of Science and Technology (KAUST), Core Labs, Thuwal, Saudi Arabia

⁵ C2P2 (CNRS-UMR 5265), Université Lyon 1, ESCPE Lyon, 43 Boulevard du 11 Novembre 1918, 69626 Villeurbanne Cedex, France

⁶King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Saudi Arabia

ABSTRACT: We report here the first step by step anchoring of a $W(\equiv C'Bu)(CH_2'Bu)_3$ complex on a highly crystalline and mesoporous MOF, namely Zr-NU-1000, using Surface organometallic Chemistry (SOMC) concept and methodology. SOMC allowed us to selectively graft the complex on the Zr₆ clusters and characterize the obtained single site material by using state of the art experimental methods including extensive solid-state NMR techniques and HAADF-STEM imaging. Further FT-IR spectroscopy revealed the presence of a W=O moiety arising from the in situ reaction of the W≡C'Bu functionality with the coordinated water coming from the 8-connected hexanuclear Zr₆ clusters. All the steps leading to the final grafted molecular complex have been identified by DFT. The obtained material was tested for gas phase and liquid phase olefin metathesis and exhibited higher catalytic activity than the corresponding catalysts synthesized by different grafting methods. This contribution establishes the importance of applying SOMC to MOF chemistry to get well defined single site catalyst on MOF inorganic secondary building units, in particular the in situ synthesis of W=O alkyl complexes from their W carbyne analogues.

INTRODUCTION

Metal Organic Frameworks (MOFs)^{1–3}, a burgeoning class of porous functional solid-state materials built with metal-based nodes (metal ions or clusters) linked by poly-topic organic ligands, are of unrivaled scientific interest in both academia ⁴ and industry.⁵ Undoubtedly, the modularity of these hybrid crystalline materials (e.g., structural and compositional diversity, tunable functionality, high surface area, adjustable pore system, etc.) renders them ideal for a wide range of application including gas storage^{6–8} and separation^{9–11}, selective smart sensing^{12–14}, ion^{15–17} and electron^{18–20} conductions, drug delivery ^{21–23} and catalysis.^{24– ²⁷ Specifically for catalysis, MOFs are gaining traction as very} well defined supports for organometallic heterogeneous catalysis and photocatalysis.^{28,29} Different strategies have emerged for the incorporation of organometallic complexes inside MOFs pores, namely through functionalized linker, unsaturated metal nodes or by simple chemisorption.²⁶

Although classical heterogeneous catalysis is the backbone of today's chemical, environmental and energy industries, it still suffers from a number of disadvantages.³⁰ Indeed, the discovery of new heterogeneous catalysts, depends significantly on trial and error strategy, rather than on a true conceptual approach. A typical example is the well-known Haber-Bosh process for ammonia synthesis which required a long pipeline of several experimental steps.^{31,32} Olefin metathesis, also

widely used in industry, was discovered in heterogeneous catalysis via the same type of trial and error approach.³³ Progressively the understanding of this reaction (coordination sphere, mechanism) came from the successful move towards well defined homogenous catalysts. Intimate mechanistic details and highly efficient catalysts for functionalized olefins culminated by the Nobel Prize in Chemistry in 2005.^{34–37} Until now, highly active heterogeneous catalysts for olefin metathesis are suffering from a relatively ill-defined material.^{38,39} To the best of our knowledge, there are a limited number of "single site" heterogeneous metathesis catalysis.^{40,41} Therefore the rational design and development of single site heterogeneous catalysts in olefin metathesis still needs to be achieved.³⁸

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60

Little progress have been made in "predictive heterogeneous catalysis" based on a reliable structure-catalytic activity relationship.⁴² However, a first step was achieved by transposing the concepts of molecular chemistry to surfaces namely by development of Surface Organometallic Chemistry (SOMC).⁴³⁻⁴⁵ After two decades of comprehensive research in SOMC, several relatively well defined active sites or surface organometallic fragment (SOMF) or surface coordination fragments (SCF) were prepared on classical silica, silica-alumina, alumina and magnesia.⁴¹ Some of these SOMF or SCF were found to be reaction intermediates in catalysis.⁴⁶ By applying these simple concepts several new reactions were discovered and existing ones were improved.^{42,47–49}

The key point of the SOMC strategy is to enter the catalytic cycle of a given reaction by a suitable pre-defined Surface Organometallic Fragment (SOMF) or a surface coordination fragment (SCF).41,50 In the SOMC strategy, the supported complex should contain in fact moieties that are selected based on the proposed mechanism derived from wellestablished elementary steps in molecular chemistry. In the case of olefin metathesis for example, it has been established that the active site is a carbene (W=C, Mo=C or Ru=C), therefore the target for the grafted complex is a carbene or another structure that can be easily activated to give a carbene. This strategy has been mainly limited to amorphous and non-crystalline silica, silica-alumina, alumina and magnesia, consequently the welldefined character of these single sites is not perfect because the surface of the solid is often ill-defined in the 2D dimension. Recent reports showed that Metal Organic Frameworks (MOFs) are undoubtedly one of the most appealing supports, 51-53 readymade to improve the single site character of the catalysts. Due to their exceptional crystallinity, porosity and surface area⁵⁴, one can precisely tune the pore size and suitably incorporate a given organometallic complex inside with the desired functionality.55 Previous tentative of using SOMF to generate well defined single site on MOFs nodes have been hindered by the lack of understanding on the interaction of the MOF supports with the organometallic complexes.^{56,57} Precisely direct functionalization of the 12-connected hexanuclear clusters on the UiO type MOFs, via their μ_3 -OH cornerstone, with d⁵ transition metal resulted mainly in non-active catalysts. However, more recent works have demonstrated that the same type of MOFs with extended pore size can be functionalized to generate highly active catalyst for different reactions including hydroboration and hydroamination.58

Additionally, in the last decade, considerable efforts devoted toward the development of stable mesoporous MOFs structures have permitted the synthesis of zirconium based MOFs, with tetra-coordinated linkers⁵⁹ among others. One reason of this extreme stability is the strong ($\eta^2 \sigma - \pi$) bond between Zr and the carboxylate ligand, whereas the mesoporosity is explained by the underlying net and the tetra-coordination of the linker providing large channels. Interestingly those Zr or Hf based MOFs markedly present terminal metal aqua and metal hydroxo bonds accessible

for the grafting of organometallic complexes in addition to the μ_3 -OH present in the case of the 12-connected hexanuclear clusters.⁶⁰ The corresponding grafted MOFs have been used for a wide range of catalytic reactions such as ethylene oligomerization with the tripodal (\equiv Hf-O-)₃Zr(CH₂Ph). Here each of the 3 different types of Hf-OH (one terminal Hf-OH, one Hf-OH₂ and one Hf- μ_3 -OH) are used to coordinate the Zr(CH₂Ph)₄ with evolution of around 3 moles of toluene.⁶¹ But the use of MOF as support for olefin metathesis catalysts is still at its early stage, ^{62–68} and to the best of our knowledge, no tungsten organometallic complex active for olefin metathesis has been grafted on MOFs via a Zr-O-W type of covalent bonding.

In the present study, we demonstrate that SOMC can be extended to MOF in the field of olefin metathesis. The organometallic compound has been selected by its strategic (SOMF) function in olefin metathesis. Precisely, W(=C'Bu)(CH₂'Bu)₃⁶⁹ was selected because it is a well-known precursor for olefin metathesis.^{70,71} Zr-NU-1000 was chosen as the MOF support, given its mesoporosity and accessible Zr aqua/hydroxo bond.^{60,72–74} Zr-NU-1000 was successfully functionalized and the obtained material was fully characterized. Strikingly, the FT-IR study revealed the formation of a W=O after grafting while the solid-state NMR and elemental analysis study confirmed the presence of a tris-neopentyl ligand around the W center. Furthermore, we performed DFT cluster calculations to understand the formation mechanism of the catalyst and periodic ab-initio simulations to probe the location of the catalytic complex inside the Zr-NU-1000 pores. Interestingly, the first-principle simulation show the grafted complexes are found to be preferentially localized in the small pores rather than in the hexagonal channels of the MOF. Remarkably, the grafted material is active in propylene metathesis reaching 250 turn over number (TON) after 16h in a flow mode even with the relatively bulky environment around the active site.

RESULTS AND DISCUSSION

Microcrystalline Zr-NU-1000 1 was synthetized according to a reported protocol,⁷⁵ thermally activated at 150°C under vacuum for 24 hours and then kept in an Argon filled glove box for future use. In a typical grafting procedure, crystalline powder of 1 was gently grinded with an excess of $W(\equiv C^{t}Bu)(CH_{2}^{t}Bu)_{3}$ 2 inside a glovebox. The resulting powder was put in a Schlenk tube which is evacuated under vacuum (<10⁻⁵ Torr), before being heated at 80°C for 24h under static vacuum. Volatile compounds were trapped under liquid nitrogen in a large reactor of 6L to quantify the neopentane (NpH) evolved. The system was then washed several times with an excess of degassed and dried pentane to remove any remaining non grafted W complex. Finally, the obtained orange powder 3 was dried under dynamic vacuum at 80°C for 24h and then fully characterized. The presence of W in 3 was quantified using ICP-atomic emission spectroscopy. The ratio W/Zr₆ was found to vary between 0.5 and 1. This means that experimentally for each Zr₆ cluster, as depicted in Figure 1, we have on average at most one complex grafted (as confirmed later by DFT). This ratio could not be further increased by varying both the reaction time and the initial molar ratio of W/Zr₆ (Supporting information Table S2). The grafting is therefore only partial, assuming the immobilization on the surface occurs by protonolysis of one Np/ Zr₆. The partial grafting was further confirmed by FT-IR spectroscopy. Indeed, in the spectrum of 3, the intensity of the band at 3674 cm⁻¹ assigned to Zr-OH ⁷⁶ significantly decreases with the W loading (Supporting information Figure S5). Additionally, new bands centered at 2954 cm⁻¹ and 896 cm⁻¹ appeared and can be assigned respectively to the v(CH) of the neopentyl ligand bonded to W and a v(W=O) frequency.77,78 For

each grafted material the gas phase analysis indicates the evolution of around 1±0.2 equivalent of NpH per grafted W which is, based on our elemental analysis data, coherent with ca. 3Np like ligands remaining around the W (Figure 2, a and b).



Figure 1: Scheme of the grafting mechanism: synthesis of supported **3** from **1** and **2**

Moreover, tungsten is uniformly dispersed in the Zr-NU-1000-W 3 as evidenced by SEM/EDS mapping (Supporting information Figures S8-S10). Next, the powder X-ray diffraction pattern (PXRD) of the Zr-NU-1000-W 3 indicates that the MOF material retains its crystallinity after grafting of W(≡CtBu)(CH2tBu)3, 2 (Figure 2c). Furthermore, the nitrogen adsorption isotherms revealed that the mesoporosity of 3 is maintained (Figure 2d) but with a decrease of the surface area from 2102 m²/g to 1607 m²/g as well as the pore volume from 1.5 to 1.2 cm³/g (Figure 2e).





Figure 2: a) Experimental values for **1** and for **3** compared to the theoretical ones for 3Np/W as depicted in **Figure 1, b)**: IR spectra of **1** (red), **3** (blue), indicating consumption of the Zr-OH bond with the loading of **2** on **1** and the appearance of the v(CH) of the neopentyl ligands and the difference **3-1** showing the appearance of the **W=O** bond at 896 cm⁻¹, **c)**: Powder X-Ray diffraction of **1** and **3** compared to the calculated PXRD from the single crystal data indicating that the framework remains crystalline after grafting, **d**): Nitrogen adsorption curves at 77K for **1** and **3** indicating reduction of the surface area after grafting of **2** on **1**, **e**): DFT pore size distribution for the initial **1** and grafted **3** calculated from the Nitrogen isotherm at 77K

2

3

4

5

6

7

8

9

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

60

We used high-angle annular dark-field scanning electron microscopy (HAADF-STEM) transmission in combination with energy-dispersive spectroscopy (EDS) to probe the locations of the tungsten species in Zr-NU-1000. 79,80 Elemental mapping by EDS could only be performed at a relatively lower magnification, the results of which show that both Zr and W are distributed throughout the entire Zr-NU-1000 crystal (Figure 3a). Interestingly, we find that the distribution of W is well aligned along with the crystal lattice of Zr-NU-1000 by superimposing the map of W on the HAADF-STEM image (Figure 3a). This observation is in agreement with our expectation that W complexes are specifically grafted on the Zr_6 10 clusters in the Zr-NU-1000 framework, instead of being randomly 11 distributed in the crystals.

12 To further confirm the site-specific anchoring of W, we acquired 13 high-resolution HAADF-STEM images for Zr-NU-1000-W along 14 the [001] and [100] directions, using a low-dose technique (see supporting information for the detailed imaging conditions). The 15 primary hexagonal channels and the smaller trigonal channels are 16 clearly identified in the [001] image (Figure 3b), and the 17 characteristic structural features of Zr-NU-1000 are also 18 recognizable in the [100] image (Figure 3c), indicating the 19 preservation of the MOF structure under our imaging conditions. 20 Notably, in both images, some lattice sites show apparently

stronger contrast (they appear as abnormally bright dots as labelled by yellow circles in the image) than the rest of the sites. Given that HAADF-STEM is highly sensitive to variations in the atomic number Z, the observed abnormally bright dots can be assigned to single-atom W species. These observations provide further evidence that W species are specifically grafted on the Zr₆ clusters, because the bright dots always coincide with the lattice sites of Zr-NU-1000, where the Zr₆ clusters are located.

Unfortunately, the resolution of our HAADF-STEM images (~ 0.7 nm) is insufficient to separate W from the Zr_6 clusters (or resolve individual Zr atoms within each cluster) that are about 0.32 nm apart from each other, and therefore they cannot allow us to differentiate the two possible structural models presented in supporting information Figure S29. Interestingly, the HAADF-STEM results imply that W is not anchored on every single available Zr₆ cluster (partial grafting for Zr-NU-1000-W-5.6%, Supporting Information Table S3), because otherwise obviously different contrast between different lattice sites would not be observed.

To further analyze the coordination sphere of the grafted tungsten complex, various solid-state NMR experiments were performed.

The ¹H magic-angle spinning (MAS) solid-state NMR spectrum of 3 exhibits resonance in the aromatic region 8.1-9.1 ppm, assigned to the protons coming from the MOF linker similarly to the parent 1 (Supporting information Figure S15). There is also a small shoulder at 3.8 ppm attributed to the remaining Zr-OH. Additionally, the spectrum of 3 displays two intense peaks centered at 0.6 and 1.4 ppm. The first one at 0.6 ppm auto-correlates in the double-quantum dimension (DQ) only (1.2 ppm in the diagonal) while the second one auto-correlates in both double and triple quantum (TQ) (2.8 and 4.2 ppm respectively) (Figure 4 a, b and c). Therefore, the strong peak at 1.4 ppm can be assigned to the CH₃ and the peak at 0.6ppm to the CH₂ of the neopentyl groups. An extra signal at -0.3 ppm was also observed and could be attributed to a bridging OH interacting both with W and Zr (Zr-OH-W).⁸¹

The ¹³C cross-polarization magic angle spinning (CP/MAS) NMR spectrum of 3 shows three new peaks compared to the spectrum of 1, at 31 ppm and 41 ppm for respectively CH₃ and C-(CH₃)₃ of the neopentyl group and a peak at around 102 ppm that could be assigned to the carbon directly linked to the metal center W-CH₂ (Figure 4). Those carbon correlated respectively with the proton peaks at 0.6 ppm and 1.4 ppm as indicated in the 2D ¹H⁻¹³C heteronuclear correlation (HETCOR) NMR spectrum. The carbon peak at 31 ppm is coherent with what have been reported on silica and for the spectra of the homogeneous complex. ⁴⁰ While for C-(CH₃)₃ and W-CH₂ both peaks are shifted by about 8 to 10ppm compared to the initial complex (Supporting information Figure S13) and what have been reported on silica support (41 and 102 ppm vs 52 and 95 ppm.), confirming the different interaction of the W complex with the MOF support. ⁴⁰ We also noticed the absence of any carbene or carbyne peak which should be at around 240 ppm and 318 ppm respectively. But this is also observed for silica and silica alumina when the complex W(\equiv C^tBu)(CH₂^tBu)₃ is not enriched with ¹³C before grafting.78 Therefore, to obtain higher quality of the ¹³C NMR spectra, the complex 2*, ¹³C labeled on the carbons attached directly to W, was prepared according to a reported procedure and grafted on 1.82 The ¹H and ¹³C solid-state NMR spectrum of 3* are similar to the ones obtained for 3, no extra peak was observed in the carbene or carbyne region (Supporting information Figure S17). The fundamental difference compared to the grafting of 2* on silica or silica alumina is obvious, where a new strong peak at 318 ppm is observed and attributed to W≡C resonance frequency.78

To explain this striking difference between the MOF support and amorphous silica, we suspected the role of coordinated water molecule close to the isolated Zr-OH. Indeed, Schrock *et al* reported the reaction of the W(\equiv C^tBu)(CH₂^tBu)₃ with water.⁸³ They showed that water could transfer hydrogen to the W=C resulting in a W=O and a W-CH₂ bond leaving the oxidation state of W unchanged and giving very stable species similarly to the one obtained for 2 in presence of water [(≡Zr-O-)W(=O)(CH₂^tBu)₃].⁸³ Furthermore, ¹H MAS and ¹³C CP MAS NMR data are in full agreement with the formation of monopodal species similar to the silica counterpart reported in the literature.84 Indeed, the coordination environment of 3 is very close to the supported species obtained by grafting of W(Cl)(=O)(CH₂^tBu)₃ on silica dehvdroxvlated at 200 °C which is stable toward the protonolysis reaction by adjacent silanols.85



Figure 3: STEM characterization of Zr-NU-1000-W. a HAADF-STEM image (left) and the corresponding EDS elemental maps (the
element type is labeled at the upper right corners) of Zr-NU-1000-W. b and c, High-resolution HAADF-STEM images of Zr-NU-1000-W
acquired along the [001] zone axis (b) and [100] zone axis (c). The raw image is shown in the left panel, and single-atom W species are
labelled by yellow circles in the right panel.



Figure 4: **a)** One-dimensional (1D) ¹H MAS solid-state NMR spectrum of **3** acquired at 600 MHz with a MAS frequency of 20 kHz, a repetition delay of 5 s, and 32 scans. **b)** Two- dimensional (2D) ¹H–¹H double-quantum (DQ)/single-quantum (SQ) and **c)** ¹H–¹H triple-quantum (TQ)/SQ NMR spectra of **3** (both acquired with 32 scans per t1 increment, a repetition delay of 5 s, and 128 individual t1 increments). **d)** ¹³C CP/MAS NMR spectrum of **3** (acquired at 9.4 T (v0 (1H) = 400 MHz) with a MAS frequency of 14 kHz, 10 000 scans, a repetition delay of 4 s, and a contact time of 2ms). **e)** 2D ¹H–¹³C CP/MAS dipolar HETCOR spectrum of **3** (acquired at 9.4 T with a MAS frequency of 14 kHz, 3000 scans per t1 increment, a repetition delay of 4 s, 64 individual t1 increments, and a contact time of typically 0.2ms



Figure 5: a) Cluster model of Zr-NU-1000 used for DFT calculations. b) Schematic representation of the adsorption of the W complex 2 on the Zr_6 nodes of Zr-NU-1000 **1** giving rise to the intermediate W1.

In order to gain more information on the grafting process and on the possible localization of the W-complex within the Zr-NU-1000-W framework, we performed DFT calculations using cluster and periodic models. Consistently with literature, the reactivity involved in the grafting of the W-complex to the Zr₆ node was modeled using a truncated cluster extracted from the X-ray structure.⁷⁶ The model we adopted for the MOF consists of a neutral cluster formed by one Zr₆ node, described with the socalled proton topology. mixed $[Zr_6(\mu_3-O)_4(\mu_3 OH_4(OH_2)_4]^{+8}$, decorated with eight benzoate groups mimicking the organic linkers (Figure 5a). To preserve the MOF structure the C and O atoms of the benzoate groups were frozen to the X-ray position throughout all the reactivity calculations. The grafting starts with adsorption of $W(\equiv C^tBu)(CH_2^tBu)_3$, 2, to the cluster representing 1, yielding intermediate W1, through interaction between the W atom and the O atom of a dangling OH group of the Zr₆ node. This step is slightly exergonic, by -3.7 kcal/mol, at the expense of a hydrogen bond between the dangling OH and a nearby H_2O (Figure 5b).

The grafting continues with a proton transfer from one Zrcoordinated H₂O molecule to one of the neopentyl groups bound to the W center, resulting in the formation of intermediate W2, presenting two Zr-OH bonds, and liberation of a neopentane molecule (Figure 6a). This highly exergonic step (-42.5 kcal/mol for W2) occurs via transition state W1-2, and a free energy barrier of 27.3 kcal/mol (Figure 7). For the sake of completeness, we also tried to transfer the proton to the W≡CtBu moiety, but the corresponding TS is located ~8.2 kcal/mol higher than W1-2 attributed to the bulkiness and rigidity of the alkynyl group (Supporting information Figure S25). Similarly, the bulkiness of **2** also prevented us to find a reasonable transition state involving the more acidic Zr-µ₃-OH proton⁸⁶ (Supporting information Figure S26). Intermediate W2 is the bifurcation point for two alternative mechanisms. One of them involving a proton transfer from one of the Zr-bound OH groups to the carbyne moiety, pathway A, the other involving transfer of the same proton to one of the neopentyl moieties, pathway B (see Figure 6b).

Along pathway A the proton transfer from one of the Zr-OH groups to the carbyne moiety of W2 leads to the W=C carbene species W3A via transition state W2-3A and a free energy barrier of 16.6 kcal/mol (Figure 7). Intermediate W3A is located 9.6 kcal/mol below W2. Another proton transfer from the remaining Zr-OH bond of W3A to the carbene moiety leads to the tri-

alkylated W-oxo intermediate W4A via transition state W3A-4A and a free energy barrier of 26.2 kcal/mol. The experimentally proposed W4A product is predicted to be at -67.3 kcal/mol, bearing delocalized W-oxo bonds. Alternatively, along pathway B the proton transfer from one of the Zr-OH groups of W2 occurs to one of the neopentyl groups, leading to intermediate W3B with liberation of a neopentane molecule, via transition state W2-3B and a free energy barrier of 17.9 kcal/mol (Figure 7). The resulting intermediate W3B is located at -74.5 kcal/mol. Pathway B is completed by another proton transfer from the remaining Zr-OH bond of W3B to the carbyne moiety, via transition state W3B-4B and a free energy barrier of 23.2 kcal/mol (Figure 7), resulting in the formation of the monoalkylated W-carbene complex W4B laying at -101.5 kcal/mol. In addition, a third pathway, pathway C (see Figure 6c) can lead to the direct formation of monoalkylated W-carbene complex W4B through transition state W3A-4B with a free energy barrier of 19.9 kcal/mol (Figure 7).

Comparison of all three pathways as presented in Figure 7 indicates that pathway A leading to the experimentally characterized species W4A, is slightly favored over pathway B, as transition state W2-3A is favored by 1.3 kcal/mol over transition state W2-3B. Considering the small energy difference between the two transition states, we calculated it using other computational approaches (Supporting Information, Table S7). While the exact value clearly depends on the specific computational protocol, we found that the energy difference between transition state W2-3A and W2-3B, is in the range between -1.4 and +1.3 kcal/mol. Nevertheless, these small energy differences indicate competition between the two pathways, and it cannot be excluded that both intermediates W3A and W3B are formed. Calculations highlight that formation of W4B is thermodynamically favored over formation of W4A (by 34.1 kcal/mol) via transition state W3A-4B (Figure 6b) having 6.3 kcal/mol lower barrier than W3A-4A. This indicates the formation of W4B is also kinetically driven since pathway C also connects to W4B as the most favorable route. Further protonation of W4B to produce bis-alkyl species W4C (Supporting information Figure S26) gives rise to a thermodynamically less stable product by 10.0 kcal/mol. Finally, analysis of the overall reaction profiles indicate that the rate determining step is the initial proton transfer from the Zr₆ cluster to the adsorbed Wcomplex, with a barrier of 27.3 kcal/mol, consistent with a reaction occurring at 80 °C over a period of 24h.

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

60

Investigation of reactivity was completed by the calculation of the ¹³C NMR chemical shifts of the C atoms of the W-complexes in the **W4A** and **W4B** products using DFT methods (Computational Details in supporting information). The predicted chemical shifts for the C(CH₃)₃, W-CH₂ and CH₃ atoms of **W4A**, 45, 82 and 37 ppm, respectively, correlate well with the three experimental peaks of **3** at 41, 102 and 31 ppm, respectively. Conversely, it is difficult to correlate the predicted chemical shifts for the C(CH₃)₃, W-CH₂ and CH₃ atoms of **W4B**, 46, 261, 58 and 34 ppm with the experimental values, which further implies the preferential formation of **W4A** during grafting.

Additional DFT calculations suggest that **W4B** can interconvert into a slightly more stable (by around 5.0 kcal/mol) W-H species preserving the oxidation state of W albeit transforming carbene into metal hydride species (Supporting information **Figure S27**). Thus, the viability of a dormant W-H species before the carbene formation but during the grafting process was also examined by considering the Np insertion into the carbene bond of intermediate **W3A**. However, the predicted free energy for the associated complex **W3A_insert** (Supporting information **Figure S27**) was 7.7 kcal/mol less stable driving the reaction backward to **W3A** to channel into **W4B**. Moreover, subsequent formation of **W4A_insert** from **W3A_insert** is still not favored over **W4B** by a free energy difference of 22.8 kcal/mol.

By and large, possible reaction mechanisms examined herein indicate that **W4B** is the only likely product under ideal conditions. However, the absence of W=CH chemical shift in the experimental NMR analysis might suggest further reaction of **W4B** through an intramolecular alkyl insertion mechanism as presented in Supporting information. Overall, any complications regarding the experimental conditions or the equilibrium towards a W-H species can lead to a complex with saturated W-C bonds consistent with NMR analysis. Further studies are ongoing to better understand the experimental selectivity for the apparently metastable **W4A** species after grafting.

Regarding the possible localization of the grafted Wcomplex within the MOF framework, we performed DFT calculations using a periodic model of Zr-NU-1000 (Supporting information **Figure S28**). The 8-connected Zr₆ clusters provide different possible grafting sites pointing toward large or small cavities. Since the surfaces of the Zr₆ nodes facing the large (31 Å) and small (10 Å) channels have similar surface functionalities, the energy difference between W-complexes grafted in different locations is mainly determined by interactions of the $W(\equiv C'Bu)(CH_2'Bu)_3$ with the pore and by the strain induced on the MOF structure to accommodate the W-complex. Consequently, we compared the grafting energy of $W(\equiv C'Bu)(CH_2'Bu)_3$ inside the small and large pores, which is the binding energy (E_b) of the resulted W moiety in W4A or W4B fashion, using:

 $E_b = E[W@NU1000] + E[NpH] - E[NU1000] - E[W];$ where E[W@NU1000], E[NU1000], E[W] and E[NpH] are the DFT computed energies for the W-grafted structure (W4A/W4B), pristine Zr-NU-1000 unit cell, the initial W(=C'Bu)(CH₂'Bu)₃ complex and neopentane molecules released.

At 0 K and at a grafting temperature of 80°C, the optimized geometries of the MOF with the grafted species as W4A in small and large pores of a unit cell are shown in the Supporting Information (Figures S29 and S33). No clear deformation is observed for both grafting modes. Inspection of the two structures, shown in different crystallographic directions highlights that the resulting W complex is essentially pointing in the [001] direction when grafted in the small cavity, whereas it is pointing in the [110] direction when grafted in the large cavity. The DFT-D3 calculated grafting electronic energy for W4A species inside the small cavity is of -90.1 kcal/mol, while it is -72.6 kcal/mol for the large one, indicating a greater stability of grafting the complex in the small pore, by around 17.5 kcal/mol. This 17.5 kcal/mol difference can be partitioned into a DFT term of 6.9 kcal/mol and a D3 term of 10.6 kcal/mol, indicating favorable dispersive interactions between the organic node linkers and the W-complex in the small cavity. Zero point energy and thermal corrections reduce this difference to 14.0 kcal/mol, still indicating a selectivity for the small pore also in terms of free energies. Further, due to steric hindrance we were able to graft only one W-complex in the small cavities (see Figure S30), which is in agreement with the experimental results of a maximum of 1W/node (Supporting Information Table S2). The DFT calculations also suggest that once one complex is grafted in the small pore, it is more favorable for the next complex to be grafted in the next neighboring small pore rather than in the site of the same Zr_6 node pointing in the larger cavity, with a difference of energy as large as 16.6 kcal mol⁻¹(Supporting Information Figures S31 and S33). Similar trends were observed when we consider the grafting resulting in the W4B species. Therefore, $W(\equiv C^{t}Bu)(CH_{2}^{t}Bu)_{3}$ anchoring on Zr-NU-1000 crystal seems to result in W-grafted species mainly localized in the small pore.



Figure 6: a) Neopentane release and formation of the bifurcation intermediate W2. b) Carbyne protonation (Pathway A) or second neopentane release (Pathway B), and alternative second neopentane release via W3A-4B (Pathway C).



Figure 7. Overview of reaction free energies along the reaction coordinate with cluster model DFT calculations.

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60



Figure 8: Catalytic performances of **3** in propene metathesis (35mg, 80°C, 20 mL.min⁻¹): **a)** black: conversion vs. time and blue: cumulated TON vs. time. **b)** Selectivity toward ethylene and butenes

Next, the activity of the well-defined single site [(\equiv Zr-O-)W(=O)(CH₂'Bu)₃] **3** was established for propylene metathesis. In a batch reactor of a known volume, 630 equivalents of propene are converted at 80°C into a thermodynamic mixtures of propylene, ethylene and 2-butene with evolution of one equivalent of neopentane per W center. This evolution of one mole of neopentane, during the reaction of **3** with propylene, is coherent with the formation of the active W carbenic sites necessary for the olefin metathesis to occur according to the Chauvin mechanism.⁸⁷ With a bulky trisneopentyl ligand, coordination of an olefin is known to favor Hydrogen transfer from the α -H to the adjacent neopentyl with elimination of neopentane and formation in situ of a neopentylidene which initiates metathesis.⁴⁰

The activity of **3** was further probed using a dynamic differential flow reactor. Around 250 accumulated turn over numbers (TON) are achieved after 16h at 80°C. Nevertheless, with the achieved TON after 16h our system shows higher activity than the recently reported Me₃Re(=O) grafted on dehydrated Zr-NU-1000 MOF, exhibiting TON of 182 after 20h.63 Additionally after the onset of the catalysis, the trans/cis 2-butene ratio is 0.70 for 3, notably lower than the silica-supported tungsten complex featuring the same local structure.⁴⁰ This can be explained by the difference of electronic properties and steric hindrance between the silica and the MOF supports that impact on the relative stabilities of the tungstacyclobutanes. Moreover the selectivity for ethylene (C_2) and 2-butene (C_4) remain constant over time on stream with an equimolar amount for both C_2 and C_4 (Figure 8). Previous experience with particularly supported tungsten system has shown that oxophilic elements, such as tungsten, are strongly attached to the surface. Therefore the deactivation of 3 might be due to a gradual decomposition of the metallacyclobutane intermediate by β -H transfer and formation of isobutene, as

observed for the supported tungsten imido system.⁸⁸ In fact, we have also observed traces of isobutene at early time on stream but this component has indeed disappeared with time. Furthermore, our DFT calculations also suggest that once the active sites are formed they can easily give hydride species resulting in catalyst deactivation (Supporting Information **Figure S27**).

In order to further explain the activity of **3** we explored the kinetic of conversion of a liquid olefin, namely 1-octene (1-C8). The catalytic conversion of 1-octene to 7-tetradecene (7-C14) is performed at 80° C at a ratio W/1-octene of around 2000 in a batch reactor. The different products that are formed during 1octene metathesis are monitored by GC and identified by GC/MS. The reaction proceeds by three distinguishable steps. Indeed we first observe an induction period of around 2 to 3h followed by a fast formation of the primary metathesis product, 7-tetradecene, with a maximum selectivity after around 5h and finally a decrease of selectivity of 7-tetradecene formation with the subsequent increase of selectivity toward the isomerization products of 1octene (2-C8, 3-C8 and 4-C8) (Supporting Information **Figure S23**).

The induction period can be explained by the progressive formation of the carbene active site which is absent in the starting pre-catalyst (vide infra). When a sufficient amount of active sites have been formed the 1-C8 metathesis to 7-C14 rapidly occurs with a high selectivity toward this primary metathesis product. After around 5h, the selectivity for 7-C14 begins to decline and simultaneously isomerization's products takes over. The catalyst starts progressively deactivating, possibly by β -H transfer, resulting in a decrease in metathesis activity and a subsequent increase in isomerization reaction. It is likely that isomerization occurs via the hydride coming from this β -H transfer.⁴⁰ The cross metathesis between 1-C8 and these isomerization products occurs also in parallel but in a lesser extent (Supporting Information Figure S23). All the expected liquid products (Supporting information Figure S22) have thus been identified by GC/MS and quantified by GC.

The reactivity of 3 for 1-octene metathesis is compared to previously reported supported catalysts employed for the selfmetathesis of 1-octene including several tungsten, molybdenum and ruthenium complexes immobilized on solid supports by adsorption^{92,93}. SOMC strategy^{89,90}, grafting⁹¹, and encapsulation^{94,95} techniques (see Supporting Information Table S4). A comparison of the catalysis data shows that, under the respective reaction conditions, the catalytic turnover obtained with 3 is generally higher than for the other reported systems. Moreover, the selectivity achieved at 5h is one the highest reported. Therefore, whereas the precursor 2 (the homogeneous W precursor is known to be inactive in olefin metathesis because of the fast bi-molecular recombination in homogeneous catalysis) and the support Zr-NU-1000 1 are both inactive under the applied conditions, the data indicate that the grafting of 2 onto 1 generates a new surface complex 3 significantly active and with good selectivity for olefin metathesis.

The discussion will be mainly focused on the actual structure of the catalyst, its localization inside the MOF and the mechanism of olefin metathesis with the grafted W complex. For that purpose, we will mention all the data obtained on this single site-single atom catalysis.

Actual structure of the pre-catalyst grafted W complex

The experimental data indicate that the structure of our "precatalyst" is $[(\equiv Zr-O-)W(=O)(CH_2^{t}Bu)_3]$ This is a surprising result given the fact that the cluster model DFT calculations indicate that $[(\equiv Zr-O-)W(=O)(CH_2^{t}Bu)_3]$ is higher in energy by 34.1 kcal/mol as compared to $[(\equiv Zr-O-)W(=O)(=CH^{t}Bu)(CH_2^{t}Bu)]$ and Environment Since the starting material is $W(\equiv C^tBu)(-CH_2^tBu)_3$, its grafting on the Zr-OH sites occurs by the addition of this Zr-OH on the $W(\equiv C^tBu)$ moiety, as suggested by the DFT calculations (**Figure 6**). One can see easily by FT-IR a strong decrease of the Zr-OH band of the Zr-NU-1000 MOF and the appearance of a W=O band at 896cm⁻¹ as well as the absence of any $W(\equiv C^tBu)$ in the ¹³C solid state NMR (**Figure 2a, Figure 4**).

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22 23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49 50

51

52

53

54

55

56

57

58

59

60

The grafting process occurs certainly by electrophilic cleavage of a W-Np bond since one observes the liberation of one mole of NpH/ mole of grafted W. The fact that only one mole of NpH is produced rather than two moles is in favor of species **W4A** and not **W4B**. If the surface species were **W4B** one should observe the liberation of two moles of NpH which is not the case. These results are consistent with what have been previously reported for the reaction of the tungsten complex 1 with water. Indeed Xue *et al* showed that 1 undergoes readily hydrolysis with the formation of a stable dinuclear (Np₃W=O)-O-(Np₃W=O) complex without further neopentane release.⁹⁶ Moreover Schrock *et al* had previously reported the reaction of the W(≡C'Bu)(CH₂'Bu)₃ with water and showed that water could transfer hydrogen to the W≡C resulting in a W=O and a W-CH₂ bond leaving the oxidation state of W unchanged and giving very stable species similar to **W4A**.⁸³

The presence of W4A species is also confirmed by different solid state NMR approaches. Even after enrichment of the starting complex with ¹³C, the expected carbene at around 200 ppm that would correspond to W4B species was not observed. Additionally ¹H MAS and ¹³C CP MAS NMR data are in good agreement with the formation of monopodal species similar to the silica counterpart reported in the literature by the grafting of W(Cl)(=O)(Np₃) on silica dehydroxylated at 200 °C which is stable toward the protonolysis reaction by adjacent silanols.^{84,85} One can then wonder why this species W4A are active in olefin metathesis, knowing that olefin metathesis requires, according to the Chauvin mechanism,⁸⁷ the presence of a metallocarbene. The answer to this question is given by the experimental fact that once the olefin is introduced on W4A, one more mole of NpH is evolved. So as it has been observed in many cases, ^{84,85,97} the coordination of propylene to W4A creates the well-known "contraction" of the Np ligands and favors the α -hydrogen transfer from one Np ligand to an adjacent one.40

We also observed that introducing EtAlCl₂ to **W4A** liberates one mole of NpH and increases the metathesis rate quite significantly (not presented in this work).

Micro-analytical data obtained on **3** do not allow a clear cut between the two structures (Supporting information **Table S2**). However, the experimental data are strikingly in good agreement with the DFT calculated ¹³C displacement and FT-IR frequencies values of **W4A** species (Supporting information **Tables S5-S6**).

The localization of the W complex

This localization was realized by electron microscopy and by periodic DFT calculations. From the HAADF-STEM images and the corresponding EDS elemental maps, it is clear that the W is localized inside the MOF (**Figure 3a**). Additionally the high-resolution HAADF-STEM images of Zr-NU-1000-W acquired along the [001] zone axis (b) and [100] zone axis (c) clearly show that the distribution of W is well aligned along with the crystal lattice of Zr-NU-1000 by superimposing the map of W on the HAADF-STEM image. This means that this geometry fits perfectly with the lattice structure of the MOF. The W is not localized randomly inside the MOF but is more precisely

localized on the lattice sites of Zr-NU-1000. The periodic DFT calculations carried out on the various grafting sites seem to indicate that the W is preferentially located inside the small cavities between two layers, rather than inside the hexagonal cavities (Supporting information **Figures S29** and **S33**).

The mechanism of propene and 1-octene metathesis

With this Zr-NU-1000-W catalyst the mechanism is then straightforward as soon as we rationalize all our data as explained before. The precursor state of the catalyst would be **W4A** which is transformed into **W4B** by addition of the olefin, and elimination of NpH. **W4B** is then the active form of the catalyst as reported by the Chauvin mechanism.

At this point one must mention that the catalytic activity in propylene and 1-octene metathesis is reasonable but not spectacular as could be expected from a well-defined single site catalyst inside a MOF structure. The reason for this low activity could be the localization of the active site, mainly in the small cavities of the MOF structure and the resulting low accessibility of the active sites by the olefin. If the complex were pointing toward the hexagonal channels, we would expect much higher activities.

CONCLUSIONS

We reported here, for the first time, the step by step anchoring of the W(\equiv C^tBu)(CH₂^tBu)₃ inside the pores of the mesoporous Zr-NU-1000 MOF using Surface Organometallic Chemistry concept and methodology. The surface complex was fully characterized using advanced solid state NMR, FT-IR, elemental analysis, HAADF-STEM and the experimental results were integrated by DFT calculations. It was observed that the initial carbyne moiety was quantitatively transformed to a W=O due to the specific surface structure of the Zr-NU-1000 cluster with the presence of strongly coordinated water molecules. Moreover the obtained $[(\equiv Zr-O-)W(\equiv O)(CH_2^{t}Bu)_3]$ complex can be effectively activated in the presence of an olefin to give the active carbene especies and showed a mild activity for olefin metathesis with good selectivity toward the primary metathesis products. The present work establishes a high control of the in situ synthesis of W=O alkyls complex from their W carbyne analogues inside MOF pores. Noticeably, a precise study of the MOF surface structure offers great potential for the rising of new type of W=O based olefin metathesis and open new doors for the establishment of a better model for the ill-defined heterogeneous catalyst currently used in industry, namely WO₃/SiO₂. A comparison of the catalysis data with various type of W based catalysts, shows that, under similar reaction conditions, the catalytic turnover obtained with 3 is generally higher than for the other reported systems.

ASSOCIATED CONTENT

Detailed procedures for the synthesis of Zr-NU-1000-W, PXRD, TGA, DRIFTs, SEM-EDS, additional structural figures from DFT, and adsorption isotherms. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>

AUTHOR INFORMATION

Corresponding Author

*<u>mohamed.eddaoudi@kaust.edu.sa</u> *jeanmarie.basset@kaust.edu.sa

Author Contributions

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

ACS Paragon Plus Environment

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56 57

58

59

60

Funding Sources

The authors gratefully acknowledge financial support from King Abdullah University of Science and Technology (KAUST), Kingdom of Saudi Arabia

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Dr. Karim Adil, Dr. Anissa Bendjeriou and Dr. Youssef Belmabkhout are thanked for fruitful discussions.

REFERENCES

- Furukawa, H.; Furukawa, H.; Cordova, K. E.; Keeffe, M. O.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. 2013. https://doi.org/10.1126/science.1230444.
- Férey, G. Hybrid Porous Solids: Past, Present, Future. Chemical Society Reviews 2008, 37 (1), 191– 214. https://doi.org/10.1039/B618320B.
- (3) Emergence of Metal-Organic Frameworks. In Introduction to Reticular Chemistry; John Wiley & Sons, Ltd, 2019; pp 1–27. https://doi.org/10.1002/9783527821099.ch1.
- (4) Editors, G.; Long, J.; Yaghi, O.; Long, J. R.; Yaghi, O.
 M. 2009 Metal Organic Frameworks Issue The Pervasive Chemistry of Metal – Organic Frameworks w. 2009, No. 5. https://doi.org/10.1039/b903811f.
- (5) Czaja, A. U.; Trukhan, N.; Müller, U. Industrial Applications of Metal–Organic Frameworks. *Chem. Soc. Rev.* 2009, 38 (5), 1284–1293. https://doi.org/10.1039/B804680H.
- (6) Li, B.; Wen, H.-M.; Zhou, W.; Xu, J. Q.; Chen, B. Porous Metal-Organic Frameworks: Promising Materials for Methane Storage. *Chem* 2016, 1 (4), 557–580.
 - https://doi.org/10.1016/j.chempr.2016.09.009.
- (7) Alezi, D.; Belmabkhout, Y.; Suyetin, M.; Bhatt, P. M.; Weselinski, L. J.; Solovyeva, V.; Adil, K.; Spanopoulos, I.; Trikalitis, P. N.; Emwas, A. H.; Eddaoudi, M. MOF Crystal Chemistry Paving the Way to Gas Storage Needs: Aluminum-Based Soc MOF for CH4, O2, and CO2 Storage. *Journal of the American Chemical Society* 2015, 137 (41), 13308–13318. https://doi.org/10.1021/jacs.5b07053.
- Jiang, J.; Furukawa, H.; Zhang, Y.-B.; Yaghi, O. M. High Methane Storage Working Capacity in Metal– Organic Frameworks with Acrylate Links. J. Am. Chem. Soc. 2016, 138 (32), 10244–10251. https://doi.org/10.1021/jacs.6b05261.
- (9) Assen, A. H.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Xue, D.; Jiang, H.; Eddaoudi, M. Ultra-Tuning of the Rare-Earth Fcu-MOF Aperture Size for Selective Molecular Exclusion of Branched Paraffins Angewandte. 2015, 14353–14358. https://doi.org/10.1002/anie.201506345.
- (10) Cadiau, A.; Adil, K.; Bhatt, P. M.; Belmabkhout, Y.; Eddaoudi, M. A Metal-Organic Framework – Based

Splitter for Separating Propylene from Propane. Science 2016, 353, 137, DOI: 10.1126/science.aaf6323.

- (11) Li, H.; Wang, K.; Sun, Y.; Lollar, C. T.; Li, J.; Zhou, H.-C. Recent Advances in Gas Storage and Separation Using Metal–Organic Frameworks. *Materials Today* 2018, 21 (2), 108–121. https://doi.org/10.1016/j.mattod.2017.07.006.
- (12) Assen, A. H.; Yassine, O.; Shekhah, O.; Eddaoudi, M.; Salama, K. N. MOFs for the Sensitive Detection of Ammonia: Deployment of Fcu-MOF Thin Films as Effective Chemical Capacitive Sensors. *ACS Sens.* 2017, 2 (9), 1294–1301. https://doi.org/10.1021/acssensors.7b00304.
- (13) Small, L. J.; Hill, R. C.; Krumhansl, J. L.; Schindelholz, M. E.; Chen, Z.; Chapman, K. W.; Zhang, X.; Yang, S.; Schröder, M.; Nenoff, T. M. Reversible MOF-Based Sensors for the Electrical Detection of Iodine Gas. ACS Appl. Mater. Interfaces 2019, 11 (31), 27982–27988. https://doi.org/10.1021/acsami.9b09938.
- (14) Kumar, P.; Deep, A.; Kim, K.-H. Metal Organic Frameworks for Sensing Applications. *TrAC Trends in Analytical Chemistry* **2015**, *73*, 39–53. https://doi.org/10.1016/j.trac.2015.04.009.
- (15) Taylor, J. M.; Dawson, K. W.; Shimizu, G. K. H. A Water-Stable Metal–Organic Framework with Highly Acidic Pores for Proton-Conducting Applications. J. Am. Chem. Soc. 2013, 135 (4), 1193– 1196. https://doi.org/10.1021/ja310435e.
- (16) Horike, S.; Umeyama, D.; Kitagawa, S. Ion Conductivity and Transport by Porous Coordination Polymers and Metal–Organic Frameworks. Acc. Chem. Res. 2013, 46 (11), 2376– 2384. https://doi.org/10.1021/ar300291s.
- (17) Yoshida, Y.; Kitagawa, H. Ionic Conduction in Metal–Organic Frameworks with Incorporated Ionic Liquids. ACS Sustainable Chem. Eng. 2019, 7 (1), 70–81.

https://doi.org/10.1021/acssuschemeng.8b05552.

- (18) Talin, A. A.; Centrone, A.; Ford, A. C.; Foster, M. E.; Stavila, V.; Haney, P.; Kinney, R. A.; Szalai, V.; Gabaly, F. E.; Yoon, H. P.; Léonard, F.; Allendorf, M. D. Tunable Electrical Conductivity in Metal-Organic Framework Thin-Film Devices. *Science* 2014, 343 (6166), 66–69. https://doi.org/10.1126/science.1246738.
- (19) Sun, L.; Campbell, M. G.; Dincă, M. Electrically Conductive Porous Metal–Organic Frameworks. *Angewandte Chemie International Edition* **2016**, 55 (11), 3566–3579. https://doi.org/10.1002/anie.201506219.
- (20) Kung, C.-W.; Otake, K.; Buru, C. T.; Goswami, S.; Cui, Y.; Hupp, J. T.; Spokoyny, A. M.; Farha, O. K. Increased Electrical Conductivity in a Mesoporous Metal–Organic Framework Featuring Metallacarboranes Guests. J. Am. Chem. Soc. 2018, 140 (11), 3871–3875. https://doi.org/10.1021/jacs.8b00605.
- (21) Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J. F.; Heurtaux, D.; Clayette,

ACS Paragon Plus Environment

P.; Kreuz, C.; Chang, J.-S.; Hwang, Y. K.; Marsaud, V.; Bories, P.-N.; Cynober, L.; Gil, S.; Férey, G.; Couvreur, P.; Gref, R. Porous Metal–Organic-Framework Nanoscale Carriers as a Potential Platform for Drug Delivery and Imaging. *Nature Materials* **2010**, 9 (2), 172–178. https://doi.org/10.1038/nmat2608.

(22) Della Rocca, J.; Liu, D.; Lin, W. Nanoscale Metal– Organic Frameworks for Biomedical Imaging and Drug Delivery. Acc. Chem. Res. 2011, 44 (10), 957– 968. https://doi.org/10.1021/ar200028a.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

- (23) Ananthoji, R.; F. Eubank, J.; Nouar, F.; Mouttaki, H.; Eddaoudi, M.; P. Harmon, J. Symbiosis of Zeolite like Metal–Organic Frameworks (Rho-ZMOF) and Hydrogels: Composites for Controlled Drug Release. *Journal of Materials Chemistry* 2011, 21 (26), 9587–9594. https://doi.org/10.1039/C1JM11075F.
- Yang, D.; Gates, B. C. Catalysis by Metal Organic Frameworks: Perspective and Suggestions for Future Research. ACS Catal. 2019, 9 (3), 1779–1798. https://doi.org/10.1021/acscatal.8b04515.
- (25) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X. Metal Organic Framework Catalysis: Quo Vadis? ACS Catalysis 2014, 4 (2), 361–378. https://doi.org/10.1021/cs400959k.
- (26) Lee, J.; K. Farha, O.; Roberts, J.; A. Scheidt, K.; T. Nguyen, S.; T. Hupp, J. Metal–Organic Framework Materials as Catalysts. *Chemical Society Reviews* 2009, 38 (5), 1450–1459. https://doi.org/10.1039/B807080F.
- Wang, C.; An, B.; Lin, W. Metal–Organic Frameworks in Solid–Gas Phase Catalysis. ACS Catal. 2019, 9 (1), 130–146. https://doi.org/10.1021/acscatal.8b04055.
- (28) Zhu, Q.-L.; Xu, Q. Metal–Organic Framework Composites. *Chemical Society Reviews* 2014, 43 (16), 5468–5512. https://doi.org/10.1039/C3CS60472A.
- (29) Samantaray, M. K.; D'Elia, V.; Pump, E.; Falivene, L.; Harb, M.; Ould Chikh, S.; Cavallo, L.; Basset, J.-M. The Comparison between Single Atom Catalysis and Surface Organometallic Catalysis. *Chem. Rev.* 2020, 120 (2), 734–813. https://doi.org/10.1021/acs.chemrev.9b00238.
- (30) Thomas, J. M.; Thomas, W. J. Principles and Practice of Heterogeneous Catalysis. 2015.
- (31) Haber, F. Thermodynamik technischer Gasreaktionen; Sieben Vorlesungen,; R. Oldenburg: Munchen, 1905.
- (32) Haber, F.; Rossignol, R. L. Über Das Ammoniak-Gleichgewicht. Berichte der deutschen chemischen Gesellschaft 1907, 40 (2), 2144–2154. https://doi.org/10.1002/cber.190704002129.
- (33) Banks, R. L.; Bailey, G. C. Olefin Disproportionation. A New Catalytic Process. *I&EC Product Research and Development* **1964**, 3 (3), 170– 173. https://doi.org/10.1021/i360011a002.
- (34) Jean-Louis Hérisson, P.; Chauvin, Y. Die Makromolekulare Chemie. *Makromol. Chem. Die Makromolekulare Chemie* **1971**, 141 (1), 161–176.

- (35) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. A Series of Well-Defined Metathesis Catalysts– Synthesis of [RuCl2(=CHR')(PR3)2] and Its Reactions. Angewandte Chemie International Edition in English 1995, 34 (18), 2039–2041. https://doi.org/10.1002/anie.199520391.
- (36) Grubbs, R. H. Handbook of Metathesis. **2015**, *1*, 33–70.
- (37) Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. Preparation and Characterization of Active Niobium, Tantalum and Tungsten Metathesis Catalysts. *Journal of Molecular Catalysis* 1980, 8 (1), 73–83. https://doi.org/10.1016/0304-5102(80)87006-4.
- (38) Lwin, S.; Wachs, I. E. Olefin Metathesis by Supported Metal Oxide Catalysts. **2014**. https://doi.org/10.1021/cs500528h.
- Lwin, S.; Li, Y.; Frenkel, A. I.; Wachs, I. E. Nature of WO x Sites on SiO2 and Their Molecular Structure – Reactivity / Selectivity Relationships for Propylene Metathesis. 2016, 3. https://doi.org/10.1021/acscatal.6b00389.
- (40) Mazoyer, E.; Merle, N.; Mallmann, A. de; Basset, J.-M.; Berrier, E.; Delevoye, L.; Paul, J.-F.; Nicholas, C. P.; Gauvin, R. M.; Taoufik, M. Development of the First Well-Defined Tungsten Oxo Alkyl Derivatives Supported on Silica by SOMC: Towards a Model of WO3/SiO2 Olefin Metathesis Catalyst. *Chem. Commun.* 2010, 46 (47), 8944. https://doi.org/10.1039/c0cc02507k.
- Basset, J.-M.; Pelletier, J. D. A. Predictive Approach of Heterogeneous Catalysis. *Natl Sci Rev* 2018, 5 (5), 633–635. https://doi.org/10.1093/nsr/nwy069.
- (42) K. Samantaray, M.; Pump, E.; Bendjeriou-Sedjerari, A.; D'Elia, V.; A. Pelletier, J. D.; Guidotti, M.; Psaro, R.; Basset, J.-M. Surface Organometallic Chemistry in Heterogeneous Catalysis. *Chemical Society Reviews* 2018, 47 (22), 8403–8437. https://doi.org/10.1039/C8CS00356D.
- (43) Basset, J.; Psaro, R.; Roberto, D.; Ugo, R.; Chemie, W. F.; De, D. O.; Wirtschaft, S.; Basset, J. M.; Ugo, R. Modern Surface Organometallic Chemistry Schnell Und Portofrei Erhältlich Bei Chemistry ". 2009.
- (44) Hugues, F.; Bassett, J. M.; Taarit, Y. B.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. Surface Organometallic Chemistry: Formation of HFe₃ (CO) ₁₁ - from Fe₃ (CO) ₁₂ and Fe(CO) ₅ on Silica, Alumina, Magnesia, and Zinc Oxide. J. Am. Chem. Soc. 1982, 104 (25), 7020–7024. https://doi.org/10.1021/ja00389a022.
- (45) Basset, J. M.; Choplin, A. Surface Organometallic Chemistry: A New Approach to Heterogeneous Catalysis? *Journal of Molecular Catalysis* 1983, 21 (1), 95–108. https://doi.org/10.1016/0304-5102(93)80113-9.
- Pelletier, J. D. A.; Basset, J.-M. Catalysis by Design: Well-Defined Single-Site Heterogeneous Catalysts. *Accounts of Chemical Research* 2016, 49 (4), 664–677. https://doi.org/10.1021/acs.accounts.5b00518.

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56 57

58

- (47) Jezequel, M.; Dufaud, V.; Ruiz-Garcia, M. J.; Carrillo-Hermosilla, F.; Neugebauer, U.; Niccolai, G. P.; Lefebvre, F.; Bayard, F.; Corker, J.; Fiddy, S.; Evans, J.; Broyer, J. P.; Malinge, J.; Basset, J. M. Supported Metallocene Catalysts by Surface Organometallic Chemistry. Synthesis, Characterization, and Reactivity in Ethylene Polymerization of Oxide-Supported Mono- and Biscyclopentadienyl Zirconium Alkyl Complexes: Establishment of Structure/Reactivity r. *Journal of the American Chemical Society* 2001, *123* (15), 3520–3540. https://doi.org/10.1021/ja000682q.
- (48) Vidal, V. Metathesis of Alkanes Catalyzed by Silica-Supported Transition Metal Hydrides. *Science* 1997, 276 (5309), 99–102. https://doi.org/10.1126/science.276.5309.99.
- (49) Le Quéméner, F.; Barman, S.; Merle, N.; Aljuhani, M. A.; Samantaray, M. K.; Saih, Y.; Szeto, K. C.; De Mallmann, A.; Minenkov, Y.; Huang, K.-W.; Cavallo, L.; Taoufik, M.; Basset, J.-M. Metathetic Oxidation of 2-Butenes to Acetaldehyde by Molecular Oxygen Using the Single-Site Olefin Metathesis Catalyst (≡SiO)2Mo(=O)2. ACS Catalysis 2018, 8 (8), 7549–7555. https://doi.org/10.1021/acscatal.8b01767.
- (50) Scott, S. L.; Basset, J.-M. Stoichiometric and Catalytic Reactivity of Organometallic Fragments Supported on Inorganic Oxides. *Journal of Molecular Catalysis* 1994, 86 (1), 5–22. https://doi.org/10.1016/0304-5102(93)E0163-B.
- (51) Ji, P.; Manna, K.; Lin, Z.; Urban, A.; Greene, F. X.; Lan, G.; Lin, W. Single-Site Cobalt Catalysts at New Zr 8 (μ 2 -O) 8 (μ 2 -OH) 4 Metal-Organic Framework Nodes for Highly Active Hydrogenation of Alkenes, Imines, Carbonyls, and Heterocycles. *Journal of the American Chemical Society* 2016, 8, jacs.6b06759. https://doi.org/10.1021/jacs.6b06759.
- (52) Zhang, Y.; Wang, Q.; Jiang, D.; Zhou, H. Systematic Engineering of Single Substitution in Zirconium Metal – Organic Frameworks toward High-Performance Catalysis. 2017. https://doi.org/10.1021/jacs.7b09553.
- (53) Canivet, J.; Aguado, S.; Schuurman, Y.; Farrusseng, D. MOF-Supported Selective Ethylene Dimerization Single-Site Catalysts through One-Pot Postsynthetic Modification. *Journal of the American Chemical Society* 2013, 135 (11), 4195–4198. https://doi.org/10.1021/ja312120x.
- (54) Eddaoudi, M.; Li, H.; Yaghi, O. M. Highly Porous and Stable Metal - Organic Frameworks : Structure Design and Sorption Properties. J. Am. Chem. Soc. 2000, 122, 1391–1397, DOI: 10.1021/ja9933386.
- (55) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; Keeffe, M. O.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. *Science* 2002, 295 (5554), 469–472, DOI:10.1126/science.1067208

- Larabi, C.; Alessandra, E. Titration of Zr3 (μ-OH) Hydroxy Groups at the Cornerstones of Bulk MOF UiO-67, [Zr 6 O 4 (OH) 4 (Biphenyldicarboxylate) 6], and Their Reaction with [AuMe (PMe 3)].
 2012, 3, 3014–3022. https://doi.org/10.1002/ejic.201200033.
- (57) Bernard, C. Surface Organometallic Chemistry on Metal Organic Frameworks (MOF): Synthesis , Characterization and Their Application in Catalysis Cherif Larabi. **2013**.
- (58) Manna, K.; Ji, P.; Greene, F. X.; Lin, W. Metal Organic Framework Nodes Support Single-Site Magnesium – Alkyl Catalysts for Hydroboration and Hydroamination Reactions. 2016, 3–6. https://doi.org/10.1021/jacs.6b03689.
- (59) Bai, Y.; Dou, Y.; Xie, L.-H.; Rutledge, W.; Li, J.-R.; Zhou, H.-C. Zr-Based Metal–Organic Frameworks: Design, Synthesis, Structure, and Applications. *Chemical Society Reviews* **2016**, 45 (8), 2327–2367. https://doi.org/10.1039/C5CS00837A.
- (60) Mondloch, J. E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; Demarco, E. J.; Weston, M. H.; Sarjeant, A. A.; Nguyen, S. T.; Stair, P. C.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. Vapor-Phase Metalation by Atomic Layer Deposition in a Metal-Organic Framework. *Journal of the American Chemical Society* 2013, 135 (28), 10294–10297. https://doi.org/10.1021/ja4050828.
- (61) Klet, R. C.; Tussupbayev, S.; Borycz, J.; Gallagher, J. R.; Stalzer, M. M.; Miller, J. T.; Gagliardi, L.; Hupp, J. T.; Marks, T. J.; Cramer, C. J.; Delferro, M.; Farha, O. K. Single-Site Organozirconium Catalyst Embedded in a Metal-Organic Framework. *Journal of the American Chemical Society* 2015, *137* (50), 15680–15683. https://doi.org/10.1021/jacs.5b11350.
- (62) Chołuj, A.; Zielinski, A.; Grela, K.; Chmielewski, M. J. Metathesis@MOF: Simple and Robust Immobilization of Olefin Metathesis Catalysts inside (Al)MIL-101-NH₂. ACS Catal. 2016, 6, 6343– 6349, DOI: 10.1021/acscatal.6b01048.
- (63) Korzynski, M. D.; Consoli, D. F.; Zhang, S.; Romanleshkov, Y.; Dinca, M.; Korzyński, M. D.; Consoli, D. F.; Zhang, S.; Román-leshkov, Y. Activation of Methyltrioxorhenium for Olefin Metathesis in a Zirconium-Based Metal-Organic Framework 2018. https://doi.org/10.1021/jacs.8b02837.
- (64) Chołuj, A.; Krzesiński, P.; Ruszczyńska, A.; Bulska, E.; Kajetanowicz, A.; Grela, K. Noncovalent Immobilization of Cationic Ruthenium Complex in a Metal–Organic Framework by Ion Exchange Leading to a Heterogeneous Olefin Metathesis Catalyst for Use in Green Solvents. *Organometallics* 2019, 38 (18), 3397–3405. https://doi.org/10.1021/acs.organomet.9b00287.
- (65) Chołuj, A.; Nogaś, W.; Patrzałek, M.; Krzesiński, P.; Chmielewski, M. J.; Kajetanowicz, A.; Grela, K. Preparation of Ruthenium Olefin Metathesis Catalysts Immobilized on MOF, SBA-15, and 13X for Probing Heterogeneous Boomerang Effect.

438.

Catalysts https://doi.org/10.3390/catal10040438. (66) Chołuj, A.; Karczykowski, R.; Chmielewski, M. J. Simple and Robust Immobilization of a Ruthenium Olefin Metathesis Catalyst Inside MOFs by Acid-Base Reaction. Organometallics 2019, 38 (18), 3392-3396. https://doi.org/10.1021/acs.organomet.9b00281. (67)Yuan, J.; Fracaroli, A. M.; Klemperer, W. G.

1

2

3

4

5

6

Convergent Synthesis a Metal–Organic of Framework Supported Olefin Metathesis Catalyst. Organometallics 2016, 35 (12), 2149-2155. https://doi.org/10.1021/acs.organomet.6b00365. Spekreijse, J.; Öhrström, L.; Sanders, J. P. M.; Bitter, (68)J. H.; Scott, E. L. Mechanochemical Immobilisation of Metathesis Catalysts in a Metal-Organic

2020,

10

(4),

- Framework. Chemistry A European Journal 2016, 22 (43), 15437-15443. https://doi.org/10.1002/chem.201602331.
- (69) Clark, D. N.; Schrock, R. R. Multiple Metal-Carbon Tungsten Bonds. 12. and Molybdenum Neopentylidyne and Some Tungsten Neopentylidene Complexes. J. Am. Chem. Soc. 1978, 100 (21), 6774-6776. https://doi.org/10.1021/ja00489a049.
- (70)Jean-Louis Hérisson, P.; Chauvin, Υ. Die Makromolekulare Chemie. Makromol. Chem. Die Makromolekulare Chemie 1971, 141 (1), 161-176.
- (71)Bendjeriou-sedjerari, A.; Sofack-kreutzer, J.; Minenkov, Y.; Abou-hamad, E.; Hamzaoui, B.; Werghi, B.; Anjum, D. H.; Cavallo, L.; Huang, K.; Basset, M. Heterogeneous Catalysis Tungsten (VI) Carbyne / Bis (Carbene) Tautomerization Enabled by N- Donor SBA15 Surface Ligands : A Solid-State NMR and DFT Study Angewandte. 2016, 11162-11166. https://doi.org/10.1002/anie.201605934.
- (72)Beyzavi, M. H.; Klet, R. C.; Tussupbayev, S.; Borycz, J.; Vermeulen, N. A.; Cramer, C. J.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. A Hafnium-Based Metal-Organic Framework as an Efficient and Multifunctional Catalyst for Facile CO2 Fixation and Regioselective and Enantioretentive Epoxide Activation. Journal of the American Chemical Society 15861-15864. 2014, 136 (45), https://doi.org/10.1021/ja508626n.
- (73) Goetjen, T. A.; Zhang, X.; Liu, J.; Hupp, J. T.; Farha, O. K. Metal–Organic Framework Supported Single Chromium(III) Catalyst for Ethylene Site Oligomerization at Low Pressure and Temperature. ACS Sustainable Chemistry & Engineering 2019, 7 (Iii), 2553-2557.

https://doi.org/10.1021/acssuschemeng.8b05524.

(74)Ikuno, T.; Zheng, J.; Vjunov, A.; Sanchez-sanchez, M.; Ortun, M. A.; Pahls, D. R.; Fulton, J. L.; Camaioni, D. M.; Li, Z.; Ray, D.; Mehdi, B. L.; Browning, N. D.; Farha, O. K.; Hupp, J. T.; Cramer, C. J.; Gagliardi, L.; Lercher, J. A. Methane Oxidation to Methanol Catalyzed by Cu-Oxo Clusters

Stabilized in NU-1000 Metal - Organic Framework. 2017. https://doi.org/10.1021/jacs.7b02936.

(75) Wang, T. C.; Vermeulen, N. A.; Kim, I. S.; Martinson, A. B. F.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. Scalable Synthesis and Post-Modification of a Mesoporous Metal-Organic Framework Called NU-1000. Nature Protocols 2015, 149-162. 11 (1), https://doi.org/10.1038/nprot.2016.001.

Planas, N.; Mondloch, J. E.; Tussupbayev, S.; (76)Borycz, J.; Gagliardi, L.; Hupp, J. T.; Farha, O. K.; Cramer, C. J. Defining the Proton Topology of the Zr6 -Based Metal-Organic Framework NU-1000. The Journal of Physical Chemistry Letters 2014, 6, 141010030645005. https://doi.org/10.1021/jz501899j.

- (77)Kress, B. J. R. M.; Russell, J. M.; Wesolek, G.; Osborn, J. A. Tungsten (VI) and Molybdenum (VI) Oxo-Alkyl Species . Their Role in the Metathesis of Olefins. J. Chem. Soc., Chem. Commun. 1980, 2 (D), 2-3.
- Roux, E. Le; Taoufik, M.; Chabanas, M.; Alcor, D.; (78)Baudouin, A.; Cope, C.; Thivolle-cazat, J. Well-Defined Surface Tungstenocarbyne Complexes through the Reaction of [W (t C t Bu)(CH 2 t Bu) 3] with Silica. 2005, No. 16, 4274-4279. https://doi.org/10.1021/om050086a.
- (79)Zhu, Y.; Ciston, J.; Zheng, B.; Miao, X.; Czarnik, C.; Pan, Y.; Sougrat, R.; Lai, Z.; Hsiung, C.-E.; Yao, K.; Pinnau, I.; Pan, M.; Han, Y. Unravelling Surface and Interfacial Structures of a Metal-Organic Framework by Transmission Electron Microscopy. Nature Materials. 2017, 16, 532-536, DOI: 10.1038/nmat4852
- Aulakh, D.; Liu, L.; Varghese, J. R.; Xie, H.; (80)Islamoglu, T.; Duell, K.; Kung, C.-W.; Hsiung, C.-E.; Zhang, Y.; Drout, R. J.; Farha, O. K.; Dunbar, K. R.; Han, Y.; Wriedt, M. Direct Imaging of Isolated Single-Molecule Magnets in Metal-Organic Frameworks. Journal of the American Chemical Society 2019. 141 2997-3005. (7), https://doi.org/10.1021/jacs.8b11374.
- (81)Cuesta, L.; Gerbino, D. C.; Hevia, E.; Morales, D.; Clemente, M. E. N.; Pÿrez, J.; Riera, L.; Riera, V.; Miguel, D.; Garcia-granda, S. Reactivity of Molybdenum and Rhenium Hydroxo-Carbonyl Complexes toward Organic Electrophiles. 2004, 1765-1777. https://doi.org/10.1002/chem.200305577.
- (82)Chabanas, M.; Baudouin, A.; Cope, C. Perhydrocarbyl Re VII Complexes : Comparison of Molecular and Surface Complexes. 2003, No. 700, 492-504. https://doi.org/10.1021/ja020136s.
- At, R. Of Tributyltin. 1983, No. 5, 7176-7177. (83) https://doi.org/10.1021/ja00362a029.
- (84)Merle, N.; Girard, G.; Popoff, N.; De Mallmann, A.; Bouhoute, Y.; Trébosc, J.; Berrier, E.; Paul, J.-F.; Nicholas, C. P.; Del Rosal, I.; Maron, L.; Gauvin, R. M.; Delevoye, L.; Taoufik, M. On the Track to Silica-Supported Tungsten Oxo Metathesis Catalysts: Input from 17O Solid-State NMR. Inorg. Chem. 2013,

55

56

57

58

59

> 60

(17), 10119–10130. https://doi.org/10.1021/ic401521m.

- (85) Bouhoute, Y.; Grekov, D.; Szeto, K. C.; Merle, N.; De Mallmann, A.; Lefebvre, F.; Raffa, G.; Del Rosal, I.; Maron, L.; Gauvin, R. M.; Delevoye, L.; Taoufik, M. Accessing Realistic Models for the WO3-SiO2 Industrial Catalyst through the Design of Organometallic Precursors. ACS Catal. 2016, 6 (1), 1-18. https://doi.org/10.1021/acscatal.5b01744.
- Klet, R. C.; Liu, Y.; Wang, T. C.; Hupp, T.; Farha, O. (86)K. Evaluation of Brønsted Acidity and Proton Topology in Zr- and Hf-Based Metal-Organic Frameworks Using Potentiometric Acid–Base Titration. 2016. 1479-1485. https://doi.org/10.1039/c5ta07687k.
- (87)Jean-Louis, P.; Hérisson Chauvin, Y. Catalyse de Transformation Des Oléfines Par Les Complexes Du Tungsten. Die Makromolekulare Chemie 1970, 141 (3487), 161-176. https://doi.org/10.1002/macp.1971.021410112.
- Solans-Monfort, X.; Copéret, C.; Eisenstein, O. Oxo (88)vs Imido Alkylidene D0-Metal Species: How and Why Do They Differ in Structure, Activity, and Efficiency in Alkene Metathesis? Organometallics 2012, 31 (19), 6812-6822. https://doi.org/10.1021/om300576r.
- (89) Maity, N.; Barman, S.; Minenkov, Y.; Ould-chikh, S.; Abou-hamad, E.; Basset, J. A Silica-Supported Monoalkylated Tungsten Dioxo Complex Catalyst Olefin Metathesis. 2018. for https://doi.org/10.1021/acscatal.7b04304.
- (90)Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M.; Lesage, A.; Emsley, L.; Sinha, A.; Schrock, R. R. Surface versus Molecular Siloxy Ligands in Well-Defined Olefin Metathesis Catalysts: [(RO)3SiOMo(=NAr)(=CHtBu)(CH2tBu)]. Angewandte Chemie International Edition 2006, 45 (8),

1216-1220. https://doi.org/10.1002/anie.200503205.

(91) Yuan, J.; Fracaroli, A. M.; Klemperer, W. G. Convergent Synthesis of a Metal - Organic Framework Supported Olefin Metathesis Catalyst. 2016.

https://doi.org/10.1021/acs.organomet.6b00365.

- (92) Yuan, J.; Townsend, E. M.; Schrock, R. R.; Goldman, A. S.; Müller, P.; Takase, M. K. Preparation of Tungsten-Based Olefin Metathesis Catalysts Supported on Alumina. Advanced Synthesis Catalysis 2011, 353 (11-12),n/a-n/a. https://doi.org/10.1002/adsc.201100200.
- (93) Yang, H.; Ma, Z.; Wang, Y.; Wang, Y.; Fang, L. Hoveyda-Grubbs Catalyst Confined in the Nanocages of SBA-1: Enhanced Recyclability for Olefin Metathesis. Chem. Commun. 2010, 46 (45), 8659-8661. https://doi.org/10.1039/C0CC03227A.
- (94) Zhang, X.; Jing, L.; Wei, L.; Zhang, F.; Yang, H. Semipermeable Organic-Inorganic Hybrid Microreactors for Highly Efficient and Size-Selective Asymmetric Catalysis. ACS Catal. 2017, 7 6711-6718. (10),https://doi.org/10.1021/acscatal.7b01659.
- (95) Yang, H.; Ma, Z.; Zhou, T.; Zhang, W.; Chao, J.; Qin, Y. Encapsulation of an Olefin Metathesis Catalyst in the Nanocages of SBA-1: Facile Preparation, High Encapsulation Efficiency, and High Activity. ChemCatChem 2013, 5, 2278-2287, DOI: 10.1002/cctc.201300021
- (96) A, D. B.; Zi-ling, X. U. E. Unusual Reaction of a Tungsten Alkylidyne Complex with Water. Formation, Characterization and Crystal Structures of Oxo Trimers. 2011, 54 (12), 1903-1908. https://doi.org/10.1007/s11426-011-4419-3.
- (97) Bouhoute, Y.; Garron, A.; Grekov, D.; Merle, N.; Szeto, K. C.; Mallmann, A. D.; Rosal, I. D.; Maron, L.; Girard, G. Well-Defined Supported Mononuclear Tungsten Oxo Species as Olefin Metathesis Pre-Catalysts. 2014. https://doi.org/10.1021/cs501294j.



