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Ethenolysis of renewable methyl oleate catalyzed by readily accessible supported group VI oxo catalysts”.

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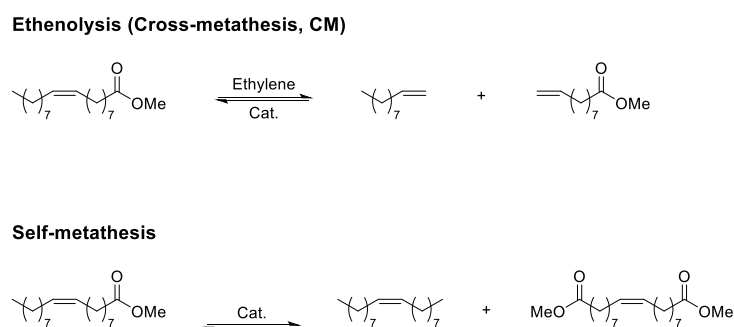
Abstract

The conversion of methyl oleate by cross-metathesis with ethylene using readily accessible supported group VI oxo species was addressed. TON up to 500 and 5000 were achieved using respectively bisgrafted tungsten- and molybdenum based systems, $(\equiv\text{SiO})_2\text{M}(=\text{O})\text{R}_2$ (M= W, R= CH_2CMe_3 , M=Mo, R= CH_2SiMe_3). In the case of molybdenum, these results are comparable to those obtained by Mo-based systems in homogeneous catalysis. Optimization studies showed that ethylene pressure plays a major role in these systems, with inhibition at high pressure resulting from degenerated metathesis involving ethylene and α -olefins.

Introduction

The production of linear α -olefins has a demonstrated industrial interest due to their utilization in a variety of applications such as co-monomer or precursor for surfactant. They are also used as starting material of a number of value added chemicals. However, their production based on fossil feedstock is dependent of the oil price volatility and on its inexorable depletion. Thus, another step forward is their production from renewable feedstock.¹ Oleochemicals, such as fatty acid monoester (FAME), are attractive bio-refinery feedstocks due to their availability on large scale at reasonable prices. Moreover, these products present multiple functional groups

allowing further chemical modifications to valuable products.^{2,3} For example, methyl oleate (MO), commonly used as a benchmark compound, obtained from transesterification of seed oils, contains an internal carbon-carbon double bond, which can react by cross metathesis reaction with ethylene to give an equimolar ratio of two α -olefins, 1-decene and methyl 9-decenoate. These products both have high commercial values. For example, methyl 9-decenoate is used in the preparation of plasticizers, lubricants, pheromones and fragrances.⁴⁻⁸ The potential of this so-called ethenolysis reaction of MO has been demonstrated with homogeneous catalysis and in particular, the moderately oxophilic ruthenium carbene bearing a cyclic alkyl amino carbene is able to reach 340,000 TON.⁹



Scheme 1. Methyl oleate ethenolysis and self-metathesis

Furthermore, early reports suggest that an increase of the conversion and quenching of self-metathesis of the ester can be achieved with an excess of ethylene (e.g., by using elevated or constant ethylene pressures).¹⁰ Nevertheless, for an industrial application, cheap, robust and recoverable catalysts are desirable. The development of catalysts based on cheaper group VI transition metal (Mo, W) is therefore of high interest. The challenge to take into account for the use of these metals is their oxophilic and highly sensitive nature. In fact, since the early report of MoI⁶ on the ethenolysis of MO by the WCl₆-Me₄Sn system, examples of the use of group VI metals are scarce. The most active system has been reported by Schrock et al. using molybdenum imido alkylidene complexes with bulky aryloxy groups (TON up to 4750) with a selectivity higher than 99% and yields up to 95%.¹¹ The tungsten analogue leads to a somewhat lower activity (TON = 310), although the selectivity remains high. Though the published Ru-based and group VI state of the art catalysts exhibit remarkable activity, the overall cost, notably the multi-step synthesis of the sophisticated ligands limits potential implementation in large scale industrial processes.

In addition, for an industrial application, use of heterogeneous catalyst not only allows an easy separation (ie. facilitates the downstream purification of the products, for instance in batch

preparation of pharmaceuticals, in which traces of metals must be removed) of the catalyst, but also avoids the bimolecular decomposition of the active center. This is particularly relevant for the ethenolysis reaction, which involves a methyldiene intermediate prone to deactivate through bimolecular coupling and reduction of the metal.¹²⁻¹⁴ Nevertheless, only few examples of heterogeneous catalysts have been published so far. They consist of rhenium oxide in combination with alkyl tin or MeReO_3 impregnated on Al_2O_3 and $\text{Al}_2\text{O}_3\text{-SiO}_2$. These catalysts display a relatively low activity.^{10,15,16} More recently, examples of immobilized ruthenium or tungsten catalysts have been reported, however they rely on the immobilization of costly organometallic precursors for a moderate activity.¹⁷⁻¹⁹ In the case of the tungsten catalyst, the authors selected an elaborated NHC-W(VI) organometallic precursor to graft on the silica surface, which somehow removes all the economical benefits of the use of this relatively cheap metal.¹⁸ Both a neutral and a cationic version of the catalyst have been tested in ethyl oleate ethenolysis and the cationic one appeared to be much more active than the neutral counterpart with a global TON of 930 after 1 h with a selectivity of 82% in cross-metathesis products, accompanied by homodimerized products, thus achieving $\text{TON} = 760$ for ethenolysis.

Thus, all the above-described systems able to efficiently perform metathesis of functionalized olefins such as MO are significantly more complex and more costly than those commonly used in industry for the metathesis of non-functionalized olefins, such as group VI metal oxides dispersed on inorganic carriers involved in major processes (OCT, Phillips...). Unfortunately, the later catalysts have so far proved to be non-reactive towards such substrates, due to the activation step (carbene formation) which requires high temperature and are thus non-adaptable for substrates containing functional groups. A breakthrough in the field would be to develop simple oxo catalysts amenable to carry out this transformation. Indeed, we have recently reported the preparation of several supported group VI alkyl oxo catalysts displaying high activity in olefin metathesis. These catalysts have been prepared using the surface organometallic methodology, which consists of the controlled chemical reaction of a surface silanol with a metal alkyl, alkoxide or halogen group. Nevertheless, we have focused our attention on the grafting of simple or easily accessible precursors. Notably, we have investigated the grafting of alkyl precursors to avoid the use of the controversial and toxic tin alkylating agents.¹⁵ We have reported the grafting of $\text{M(=O)R}_3\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{-CH}_2\text{CMe}_3$ (Np) or $\text{-CH}_2\text{SiMe}_3$ (Ns)) precursors for which we have optimized the synthesis, rendering them accessible on large scale with a stepwise, one-pot synthesis from M(=O)Cl_4 ($\text{M} = \text{Mo}, \text{W}$). For the tungsten system, $\text{W(=O)Np}_3\text{Cl}$ only leads to the formation of a monopodal species

$(\equiv\text{SiO})\text{W}(=\text{O})\text{Np}_3$, independently from the dehydroxylation temperature of the silica carrier, while $\text{W}(=\text{O})\text{Ns}_3\text{Cl}$ gives a monopodal $(\equiv\text{SiO})\text{W}(=\text{O})\text{Ns}_3$ or a bipodal species $(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$ according to the choice of the support dehydroxylation temperature.^{20–24} Furthermore, the monopodal tungsten oxo tris neosilyl surface species can react with one equivalent of phenol such as 2,6-dimethylphenol to conveniently give a modified catalyst $(\equiv\text{SiO})\text{W}(=\text{O})\text{Ns}_2(\text{OC}_6\text{H}_3\text{Me}_2)$.²⁵ More importantly, $\text{Mo}(=\text{O})\text{Np}_3\text{Cl}$ provides directly the well-defined bipodal surface species $(\equiv\text{SiO})_2\text{Mo}(=\text{O})\text{Np}_2$ when grafted onto a silica dehydroxylated at 200 °C.^{26,27} This material was shown to be active in olefin metathesis reactions for functional substrates. Herein, we report the use of simple supported group VI metal catalysts bearing only an oxo ligand and alkyl ligands (Chart 1) in the ethenolysis of MO.

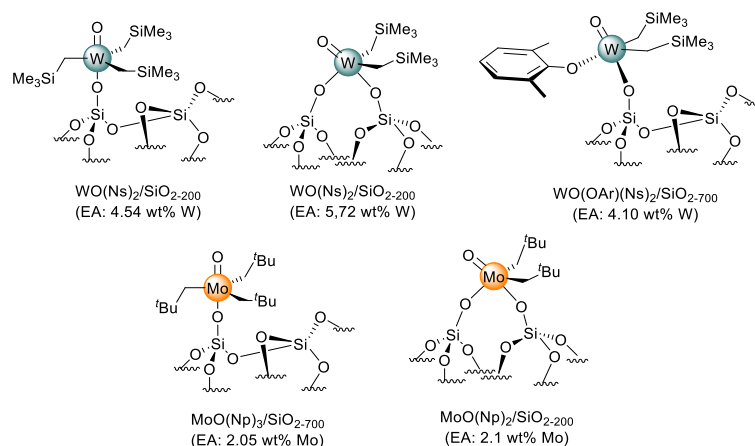


Chart 1. Supported pre-catalysts used for ethenolysis of MO.

Results and discussion

First a screening of the catalysts at 100 °C, 10 bar shows that the monopodal species $(\equiv\text{SiO})\text{W}(=\text{O})\text{Ns}_3$ is far less active than the bipodal surface species (Table 1, entry 1 and 3). Only a TON of 3 was reached after 1 h with the monopodal species, whereas a TON of 65 was obtained with the same conditions with the bipodal species $(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$ (Table 1, entry 2 and 5). This result is consistent with our previous study where a faster activation and a higher activity were reported for the bipodal species in propylene self-metathesis.²³ The longer induction period observed for the monopodal species was attributed to the steric hindrance due to the presence of three neosilyl ligands that prevents the initial coordination of propylene to the metal center, essential to trigger the alkylidene formation by α -H abstraction. This shows the subtle balance needed to optimize the formation of the active center from these pre-catalysts. Finally, the $(\equiv\text{SiO})\text{W}(=\text{O})\text{Ns}_2(\text{OAr})$ surface species having a similar coordination sphere than

$(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$ is only half as active with a TON of 220 versus 520 for $(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$ after 15 h with similar reaction conditions (Table 1, entry 2 and 5). Again these results are consistent with the fact that the bipodal species is more efficient than the modified monopodal surface species for propylene self-metathesis.²⁵

From preliminary results we have determined that the most efficient supported tungsten catalyst for the ethenolysis of MO is obtained from the bipodal $(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$ pre-catalyst. Further studies have shown that the TON increases with respect to reaction time (Figure S1, Table S1). An extensive kinetic study reveals that the initial conversion is rather low, with a virtually linear increase in conversion until 5 hours. Then, the conversion converges towards 52%. However, under these conditions the selectivity in cross metathesis (ethenolysis or CM, scheme 1) is lower at low reaction time (until 3 hours). This observation could be due to self-metathesis reaction of MO rapidly operating before the addition of ethylene. A selectivity up to 95% in cross-metathesis products is reached after 5 hours.

Table 1. Conversion, cross-metathesis selectivity (CM) and TON in MO ethenolysis with supported W catalysts

entry	catalyst	MO:W ratio	time (h)	conv. (%)	CM Sel. ^a (%)	TON
1	$(\equiv\text{SiO})\text{W}(=\text{O})\text{Ns}_3$	100	1	3	92	3
2	$(\equiv\text{SiO})\text{W}(=\text{O})\text{Ns}_2(\text{OAr})$	1000	15	22	94	220
3	$(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$	100	1	65	90	65
4	$(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$	1000	1	14	80	140
5	$(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$	1000	15	52	95	520

MO ethenolysis (T = 100 °C; initial $P_{\text{C}_2\text{H}_4}$ = 10 bar), ^a selectivity in cross metathesis.

The effect of the temperature was also evaluated with a MO/W ratio of 1000 and an ethylene pressure of 10 bar. Three temperatures were tested, namely 100, 150 and 200 °C. As observed in Figure 1 and Table S1 at short reaction times (ca. 1 h) an increase of the conversion is observed with the raising of the reaction temperature. However, when a drastic increase of the conversion is observed from 100 to 150 °C, only a small conversion rise is seen when the temperature is further increased to 200 °C. The temperature has also a beneficial effect on the selectivity in cross metathesis. In fact, the selectivity at 150 °C after 1 h reaches 95%. However, the kinetic study at the three temperatures reveals different behaviors. At 100 °C the conversion increases continuously to reach a value around 50% after 15 h. The extended reaction time also allows to reach a selectivity in CM of 95%. At 150 °C and 200 °C a similar conversion around 50% is reached in only 1 h, but no further MO was converted with a longer reaction time (ca. 5 h). This might be either due to a deactivation of the catalysts or to the presence of notable

amount of α -olefins (1-decene, ethylene), rendering the degenerated metathesis reactions more dominant and thus inhibiting the desired metathesis reaction.²⁸

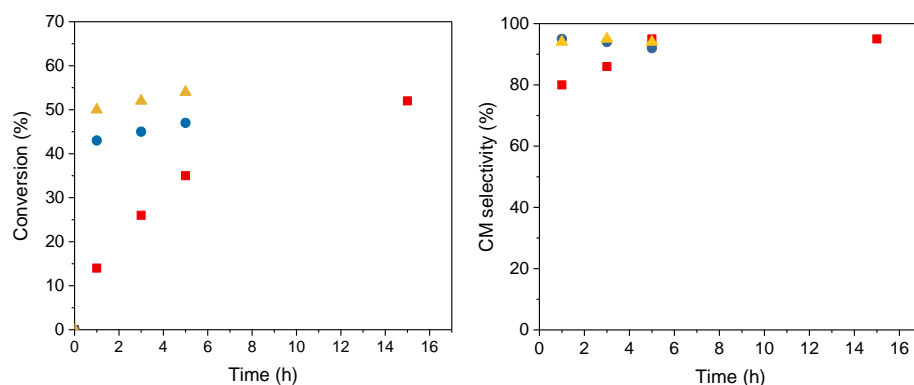


Figure 1: Conversion (left) and selectivity (right) of MO ethenolysis at 100 (■), 150 (●) and 200 °C (▲) (Catalyst: $(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$, MO/W=1000; initial $\text{P}_{\text{C}_2\text{H}_4}$ = 10 bar)

Another important reaction parameter that can strongly affect the catalytic performance is the ethylene pressure. As a large excess of ethylene is expected to favor the cross-metathesis of MO against the MO self-metathesis, we investigated the effect of the initial ethylene pressure from 2 to 30 bar after 3 hours reaction time on the conversion and selectivity (Figure 2, Figure S2 and S3).

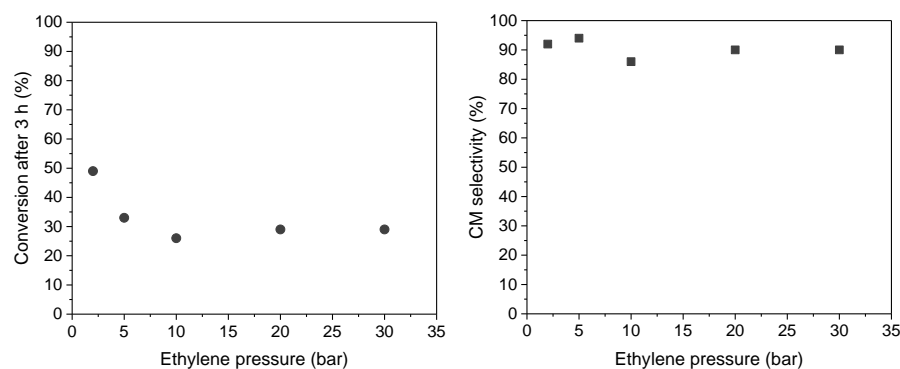


Figure 2: Conversion (left) and selectivity (right) at 3 h of MO ethenolysis in function of the initial ethylene pressure (Catalyst: $(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$, MO/W=1000; T = 100 °C)

No significant influence of the conversion is observed for pressures above 10 bar. Contrarily, higher conversion is observed for lower initial ethylene pressure. On the other hand, the selectivity in cross-metathesis products is practically independent on the ethylene pressure. This finding follows the opposite trend of that observed with Grubbs first generation catalysts for which a study has shown that varying the ethylene pressure from 1 to 16 bar does not have a

significant impact on the initial activity but leads to higher final conversion.²⁸ More importantly, contrary to what is observed with these ruthenium systems, the pressure has a small effect on the selectivity for the supported tungsten catalysts. Low pressure experiment with high selectivity can only be achieved with a micro-chemical system.³⁰ As the ethylene pressure holds a clear influence on catalytic performances, a major issue is the drop of pressure accompanying increasing conversion, which influences the reaction outcome. Thus, in order to clearly assess the effect of ethylene pressure on this tungsten-based catalytic system, ethenolysis was performed under constant pressure. Overall, five kinetic studies have been run by varying the pressure from 0.5 to 10 bar (Figure S4). As seen in Figure 3, the conversion increases from 0.5 to 5 bar and then decreases at 10 bar. Thus, 5 bar corresponds to the optimum condition. The selectivity remains unchanged (over 95 %) when an ethylene pressure higher than 2 bar is applied. The lower conversion and selectivity obtained at 0.5 and 1 bar are probably due to lower concentrations of ethylene in toluene, which is detrimental to reaction kinetics. At 10 bar ethylene concentration appears to be too high: The decrease in conversion is probably due to the ethylene degenerated self-metathesis which is occupying catalytic sites in non-productive metathesis. At such a pressure, degenerated metathesis reactions take over, involving ethylene alone and/or ethylene and α -olefins, as reported in the case of Ru-catalysts.²⁸ After 15 h reaction, the conversion obtained at 1, 2 and 5 bar are fairly similar.

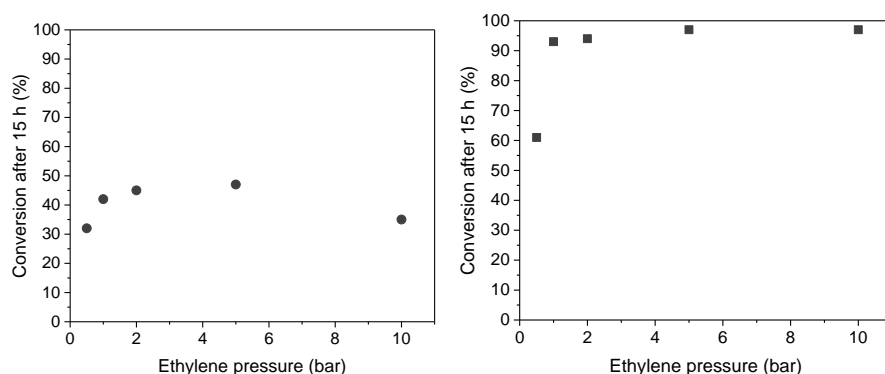


Figure 3: Conversion (left) and selectivity (right) at 15 h of MO ethenolysis in function of the constant ethylene pressure (Catalyst: $(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$, MO/W=1000; T = 100 °C)

One of the concerns of MO cross-metathesis is the possible inhibition of the catalyst by the ester function. To delineate the influence of the functional group, the ethenolysis of octadecene was performed with the optimized reaction conditions (9-octadecene/W = 1000, 100 °C, constant ethylene pressure of 5 bar). The conversion reaches 24% after 3 hours with a high selectivity that decreases over time as isomerization is occurring (Figures S1 and S5). The

conversion of the non-functionalized substrate is therefore lower than that of the MO under the same reaction conditions. This indicates that the ester function has no detrimental effect on catalytic site activity. This result reveals that in this system, activity is limited by degenerated metathesis processes involving 1-decene and ethylene as in the case of ruthenium.^{28,29}

After this promising study on supported tungsten oxo alkyl catalysts, we were interested to evaluate their molybdenum analogues, which have proven to be tolerant to functional groups and more active in propylene self-metathesis at lower temperature.^{26,27} As noticed for the tungsten system, the bipodal surface species $(\equiv\text{SiO})_2\text{Mo}(=\text{O})\text{Np}_2$ is more active even when the reaction temperature is increased in the case of the monopodal species $(\equiv\text{SiO})\text{Mo}(=\text{O})\text{Np}_3$ to favor the carbene formation by α -H abstraction.²⁰ Regarding the bipodal surface species, this system being efficient at lower temperature, only a marginal increase of the activity is observed when the reaction is performed at 50 °C instead of room temperature (ca. 25 °C). In fact, for a MO/Mo ratio of 1000 and a constant ethylene pressure of 5 bar, a conversion of 67% is reached at 50 °C while a conversion of 63% is obtained at 25 °C both with a CM selectivity around 90%. Nevertheless, for convenience, with our reactor, further experiments have been performed at 50 °C in order to study the effect of pressure. The effect of ethylene pressure was also evaluated on this molybdenum system (Figure 4). As in the case of the tungsten analogue the conversion and the selectivity are dependent on the ethylene pressure. The optimum pressure to reach a high conversion with a high selectivity is found to be 5 bar. Beneath this pressure the selectivity is below 90% whereas at a higher pressure the conversion drops. With all the experimental conditions optimized, the ratio of MO/Mo was changed (Figure S6), in order to improve the TON. It can be emphasized that even if the conversion decreases with an increasing MO/Mo ratio, a TON close to 5000 can be reached after 15 h with a MO/Mo ratio of 20,000 with an ethylene pressure of only two bar. The limited value for conversion of methyl oleate observed here can originate from two separate causes: predominance of degenerated metathesis reaction between α -olefins and ethylene (as evidenced above), or catalyst deactivation. The latter can be due to causes intrinsic to the catalysts (for instance by reduction of the metal center), or to reaction with impurities from the feed. Indeed, experiments with lower catalyst loadings show that under demanding conditions (such as in Figure S6, with substrate/catalyst ratio up to 20000), catalyst deactivation can most likely be ascribed to degradation resulting from feed impurities. Further studies will be targeted at elucidating the cause for this limit in conversion under various reaction conditions.

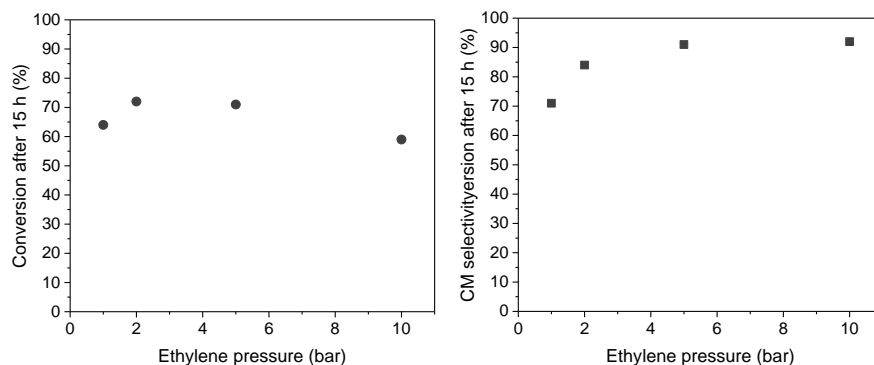


Figure 4: Conversion (left) and selectivity (right) of MO ethenolysis in function of the constant ethylene pressure (Catalyst: $(\equiv\text{SiO})_2\text{Mo}(=\text{O})\text{Np}_2$, MO/Mo =1000; T = 50 °C)

Conclusion

In this study, the issue of the conversion of a typical fatty acid methyl ester into α -olefins by ethenolysis was addressed. As this reaction has been identified as a promising route within biorefinery processes to afford a sustainable access into such compounds, the use of supported group VI oxo species presenting a low cost and an easy synthetic access, was explored. By circumventing the activation step of the oxo moiety thanks to the presence of alkyl groups on the metal center (compared to classical bis oxo species), good catalytic performances were achieved. The best tungsten-based system, $(\equiv\text{SiO})_2\text{W}(=\text{O})\text{Ns}_2$, afforded above 500 TON, while the Mo-based catalysts, $(\equiv\text{SiO})_2\text{Mo}(=\text{O})\text{Np}_2$, afforded higher productivity, with 5000 TON, which is comparable to the state-of-the art molecular catalysts based on group VI. This opens the way to future exploitation of these grafted catalysts on an industrial scale. Optimization studies showed that ethylene pressure plays a major role in these systems, with inhibition at high pressure resulting from degenerated metathesis involving ethylene and α -olefins, 1-decene in particular. For a most suitable approach to tackle this issue and improve the catalytic systems performance, the use of a continuous process is envisioned, where the α -olefin products would be constantly extracted from the reaction mixture.

Experimental

All experiments were carried out by using standard Schlenk and glove-box techniques. Ethylene (Air Liquide, 99.95%) was dried and deoxygenated before use by passing it through freshly

regenerated molecular sieves (3Å) from Aldrich and R-3-15 catalysts (BASF). Methyl oleate (99%, from Nu-Chek-Prep, Inc.) was degassed, stored over Al(*i*Bu)₃/SiO₂ and distilled prior use. Toluene was dried over Na and distilled. Silica supports were received from Evonik. SiO₂₋₂₀₀ and SiO₂₋₇₀₀ were prepared from Aerosil silica (Evonik, specific area of 200 m².g⁻¹), which was dehydroxylated at 200 and 700 °C respectively under high vacuum (10⁻⁵ Torr) for 15 h to give a white solid having a specific surface area of 190 m².g⁻¹ and containing 2.3 and 0.7 OH nm⁻² respectively. (≡SiO)W(=O)Ns₃, (≡SiO)W(=O)Ns₂(OC₆H₃Me₂), (≡SiO)₂W(=O)Ns₂, (≡SiO)Mo(=O)Np₃ and (≡SiO)₂Mo(=O)Np₂ were prepared according to published methods.^{21-23,25-27} Elemental analyses were performed at the Pascher Mikroanalytisches Labor at Remagen-Bandorf (Germany). IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF₂ windows. The samples were prepared under argon within a glove-box. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm⁻¹).

General procedure for MO ethenolysis catalytic tests at R = 1000

MO ethenolysis catalytic tests have been performed using a 60 mL autoclave in 7 mL of dry toluene. In a glove box toluene, MO (1.38 g; 4.65 mmol) and the scavenger Al(*i*Bu)₃/SiO₂ (200 mg; 0.156 mmol Al) are gently mixed together before adding the appropriate amount of catalyst. The autoclave is sealed then taken out from the glove box. The desired initial or constant ethylene pressure is introduced in the autoclave then the reaction is heated at the desired temperature under stirring (200 rpm). After catalysis, the autoclave is cooled to RT in an ice bath then slowly depressurized. 1 mL of methanol is added then all the reaction mixture is transferred into a vial. Walls of the autoclave were rinsed with around 10 mL of toluene/MeOH (95/5). Around 400 mg (precisely weighed) of tetradecane is added as the external standard then the slurry is passed through a frit. The solid is washed with 30 mL of toluene/MeOH (95/5) then the filtrate is injected in GC. Conversion is calculated from the consumption of MO determined using the tetradecane as external standard. The TON is calculated with the formula $TON = (Conversion * (Substrate/M)) / 100$. The molar selectivity in cross metathesis products (CM selectivity) is obtained from the production of 1-decene, methyl 9-decenoate (CM products), 9-octadecene, 1,18-dimethyl 9-octadecendioate (SM products) determined using the tetradecane as external standard (for example: Sel(1-decene) % = $N(\text{mol 1-decene}) / \sum \text{mol}(1\text{-decene, methyl 9-decenoate, 9-octadecene, 1,18-dimethyl 9-octadecendioate}) * 100\%$).

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Conflict of interest

This study was partly financed by Total Chemicals. Part of this work were patented (Taoufik, M.; Gauvin, R. M.; Delevoye, L.; Rouge, P.; Szeto, K. C.; Bouhoute, Y.; Strub, H. Catalytic ethenolysis of optionally-functionalized internal unsaturated olefins, Patent WO2017013062A3, 2017).

References

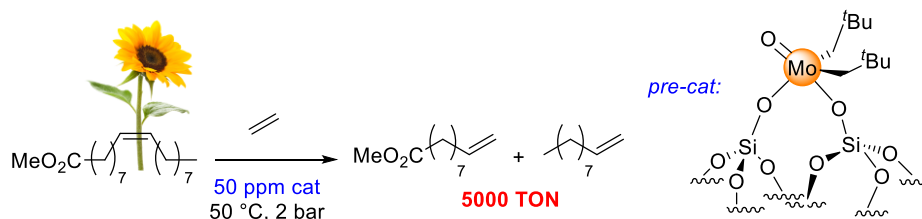
- (1) Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *Chem. Rev.* **2007**, *107*, 2411–2502.
- (2) Gunstone, F. D. Supplies of Vegetable Oils for Non-Food Purposes. *Eur. J. Lipid Sci. Technol.* *113*, 3–7.
- (3) Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. Oils and Fats as Renewable Raw Materials in Chemistry. *Angew. Chem. Int. Ed.* *50*, 3854–3871.
- (4) Spekrijse, J.; Sanders, J. P. M.; Bitter, J. H.; Scott, E. L. The Future of Ethenolysis in Biobased Chemistry. *ChemSusChem* **2017**, *10*, 470–482.
- (5) Bidange, J.; Fischmeister, C.; Bruneau, C. Ethenolysis: A Green Catalytic Tool to Cleave Carbon–Carbon Double Bonds. *Chem. – Eur. J.* **2016**, *22*, 12226–12244.
- (6) Mol, J. C.; Buffon, R. Metathesis in Oleochemistry. *J. Braz. Chem. Soc.* **1998**, *9*, 1–11.
- (7) Mol, J. C. Application of Olefin Metathesis in Oleochemistry: An Example of Green Chemistry. *Green Chem.* **2002**, *4*, 5–13.
- (8) Mol, J. C. Catalytic Metathesis of Unsaturated Fatty Acid Esters and Oils. *Top. Catal.* **2004**, *27*, 97–104.
- (9) Marx, V. M.; Sullivan, A. H.; Melaimi, M.; Virgil, S. C.; Keitz, B. K.; Weinberger, D. S.; Bertrand, G.; Grubbs, R. H. Cyclic Alkyl Amino Carbene (CAAC) Ruthenium Complexes as Remarkably Active Catalysts for Ethenolysis. *Angew. Chem. Int. Ed.* **2015**, *54*, 1919–1923.
- (10) Bosma, R. H. A.; Aardweg, F. van den; Mol, J. C. Cometathesis of Methyl Oleate and Ethylene; a Direct Route to Methyl Dec-9-Enoate. *J. Chem. Soc. Chem. Commun.* **1981**, 1132–1133.
- (11) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. Ethenolysis Reactions Catalyzed by Imido Alkylidene Monoaryloxo Monopyrrolide (MAP) Complexes of Molybdenum. *J. Am. Chem. Soc.* **2009**, *131*, 10840–10841.
- (12) Bailey, G. A.; Foscatto, M.; Higman, C. S.; Day, C. S.; Jensen, V. R.; Fogg, D. E. Bimolecular Coupling as a Vector for Decomposition of Fast-Initiating Olefin Metathesis Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 6931–6944.

- (13) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. Reduction of Molybdenum Imido-Alkylidene Complexes in the Presence of Olefins to Give Molybdenum(IV) Complexes. *Organometallics* **1991**, *10*, 2902–2907.
- (14) Lopez, L. P. H.; Schrock, R. R. Formation of Dimers That Contain Unbridged W(IV)/W(IV) Double Bonds. *J. Am. Chem. Soc.* **2004**, *126*, 9526–9527.
- (15) Sibeijn, M.; Mol, J. C. Ethenolysis of Methyl Oleate over Supported Re-Based Catalysts. *J. Mol. Catal.* **1992**, *76*, 345–358.
- (16) Mandelli, D.; Jannini, M. J. D. M.; Buffon, R.; Schuchardt, U. Ethenolysis of Esters of Vegetable Oils: Effect of B₂O₃ Addition to Re₂O₇/SiO₂.Al₂O₃-SnBu₄ and CH₃ReO₃/SiO₂.Al₂O₃ Metathesis Catalysts. *J. Am. Oil Chem. Soc.* **1996**, *73*, 229–232.
- (17) Nieres, P. D.; Zelin, J.; Trasarti, A. F.; Apesteguía, C. R. Heterogeneous Catalysis for Valorisation of Vegetable Oils via Metathesis Reactions: Ethenolysis of Methyl Oleate. *Catal. Sci. Technol.* **2016**, *6*, 6561–6568.
- (18) Pucino, M.; Mougél, V.; Schowner, R.; Fedorov, A.; Buchmeiser, M. R.; Copéret, C. Cationic Silica-Supported N-Heterocyclic Carbene Tungsten Oxo Alkylidene Sites: Highly Active and Stable Catalysts for Olefin Metathesis. *Angew. Chem. Int. Ed.* **2016**, *55*, 4300–4302.
- (19) Hübner, S.; de Vries, J. G.; Farina, V. Why Does Industry Not Use Immobilized Transition Metal Complexes as Catalysts? *Adv. Synth. Catal.* **2016**, *358*, 3–25.
- (20) 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*, 8944–8946.
- (21) 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**, *52*, 10119–10130.
- (22) 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*, 1–18.
- (23) Grekov, D.; Bouhoute, Y.; Szeto, K. C.; Merle, N.; De Mallmann, A.; Lefebvre, F.; Lucas, C.; Del Rosal, I.; Maron, L.; Gauvin, R. M.; Delevoye, L.; Taoufik, M. Silica-Supported Tungsten Neosilyl Oxo Precatalysts: Impact of the Podality on Activity and Stability in Olefin Metathesis. *Organometallics* **2016**, *35*, 2188–2196.
- (24) Larabi, C.; Szeto, K. C.; Bouhoute, Y.; Charlin, M. O.; Merle, N.; Mallmann, A. D.; Gauvin, R. M.; Delevoye, L.; Taoufik, M. Solvent-Free Ring-Opening Metathesis Polymerization of Norbornene over Silica-Supported Tungsten-Oxo Perhydrocarbyl Catalysts. *Macromol. Rapid Commun.* **2016**, *37*, 1832–1836.
- (25) Bouhoute, Y.; Rosal, I. D.; Szeto, K. C.; Merle, N.; Grekov, D.; Mallmann, A. D.; Roux, E. L.; Delevoye, L.; Gauvin, R. M.; Maron, L.; Taoufik, M. Modification of Silica-Supported Tungsten Neosilyl Oxo Precatalysts: Impact of Substituted Phenol on Activity and Stability in Olefin Metathesis. *Catal Sci Technol* **2016**, *6*, 8532–8539.
- (26) Merle, N.; Le Quémener, F.; Bouhoute, Y.; Szeto, K. C.; De Mallmann, A.; Barman, S.; Samantaray, M. K.; Delevoye, L.; Gauvin, R. M.; Taoufik, M.; Basset, J. M. Well-Defined Molybdenum Oxo Alkyl Complex Supported on Silica by Surface Organometallic Chemistry: A Highly Active Olefin Metathesis Precatalyst. *J. Am. Chem. Soc.* **2017**, *139*, 2144–2147.
- (27) Merle, N.; Quémener, F. L.; Barman, S.; Samantaray, M. K.; Szeto, K. C.; Mallmann, A. D.; Taoufik, M.; Basset, J.-M. Well-Defined Silica Supported Bipodal Molybdenum

Oxo Alkyl Complexes: A Model of the Active Sites of Industrial Olefin Metathesis Catalysts. *Chem. Commun.* **2017**, 53, 11338–11341.

- (28) Burdett, K. A.; Harris, L. D.; Margl, P.; Maughon, B. R.; Mokhtar-Zadeh, T.; Saucier, P. C.; Wasserman, E. P. Renewable Monomer Feedstocks via Olefin Metathesis: Fundamental Mechanistic Studies of Methyl Oleate Ethenolysis with the First-Generation Grubbs Catalyst. *Organometallics* **2004**, 23, 2027–2047.
- (29) Miyazaki, H.; Herbert, M. B.; Liu, P.; Dong, X.; Xu, X.; Keitz, B. K.; Ung, T.; Mkrtumyan, G.; Houk, K. N.; Grubbs, R. H. Z-Selective Ethenolysis with a Ruthenium Metathesis Catalyst: Experiment and Theory. *J. Am. Chem. Soc.* **2013**, 135, 5848–5858.
- (30) Park, C. P.; Van Wingerden, M. M.; Han, S.-Y.; Kim, D.-P.; Grubbs, R. H. Low Pressure Ethenolysis of Renewable Methyl Oleate in a Microchemical System. *Org. Lett.* **2011**, 13, 2398–2401.

Graphical abstract:



Readily accessible molybdenum oxo supported catalysts prepared from surface organometallic approach afford high performance in the ethenolysis of biosourced methyl oleate, with productivity comparable to the state-of-the art molecular group 6 catalysts.