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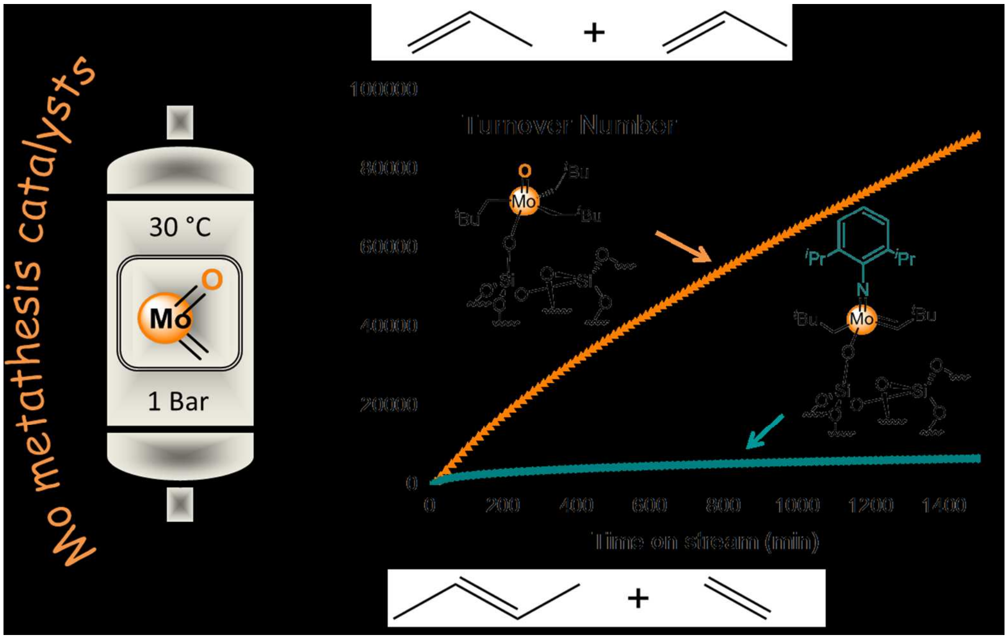

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Well defined molybdenum oxo alkyl complex supported on silica by surface organometallic chemistry: A highly active olefin metathesis precatalyst

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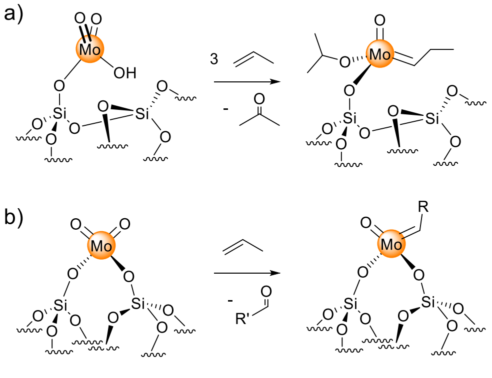
ABSTRACT: The well-defined, silica-supported molybdenum oxo alkyl species, (□SiO-)MoO($CH_2{}^tBu$)$_3$ was selectively prepared by grafting of $MoO(CH_2{}^tBu)_3Cl$ onto partially dehydroxylated silica (silica $_{700}$) using the surface organometallic chemistry approach. This surface species was fully characterized by elemental analysis, DRIFT, solid state NMR, and EXAFS spectroscopy. This new material, is related to the active species of industrial supported MoO_3/SiO_2 olefin metathesis catalysts. It displays very high activity in propene self-metathesis at room temperature (TON = 90 000 after 25 h). Remarkably, its catalytic performances outpace those of the parent imido derivative and of its tungsten oxo analogue.

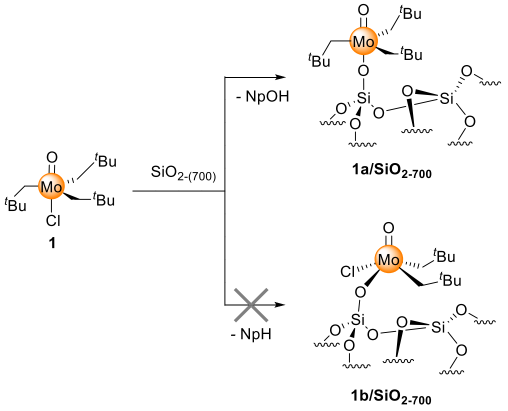
Olefin metathesis has become a powerful tool in a number of chemical transformations either in fine chemistry or in large scale industrial processes such as propylene production by the ABB Lummus OCT process using WO_3/SiO_2 or the transformation of ethylene into C_{11}-C_{14} olefin using the Shell Higher olefin process.[1] This later involves oligomerization, isomerization and olefin metathesis reactions using oxide supported-MoO_3. In fact, supported molybdenum oxides have proven to be more effective than their tungsten counterparts for the metathesis of terminal olefins higher than propene.[2] These catalysts also perform at lower temperatures (ca. 25-200 °C).[3] Supported MoO_3 catalysts feature different type of surface metallic species (monomeric, oligomeric, and clustered molybdates) that led to the proposal of several activation pathways from monopodal or bipodal surface species.[4,5,6] Trunschke et al. suggested, on the basis of IR, Raman spectroscopy and microcalorimetry studies of the activation of dispersed MoO_3 on SBA-15 that the active species arises from a monopodal bis oxo hydroxide species, which gives, in presence of propylene, a monopodal isopropoxyl molybdenum oxo carbene with the concomitant release of an acetone molecule (Scheme 1).[4] However, the actual active species has also been stated to be an isolated bipodal molybdenum oxo carbene surface species.[7,3,5] Recent works from Stair et al. bring more experimental evidence regarding the role of the isolated bipodal bis oxo molybdenum surface species that can be transformed into molybdenum carbene species by pseudo-Wittig reaction with release of aldehydes.[6] Importantly, such catalysts can be easily regenerated by treatment at high temperature under a flow of inert gas. In addition, the high temperature pretreatment required for activation could cause surface restructuration as observed by in situ EXAFS and Raman spectroscopy in the case of WO_3/SiO_2, where mono oxo species are converted into bis oxo species. The latter phenomenon brings even more difficulties for the study of this activation process.[8,9]



Scheme 1. Proposed active species of industrial Mo-catalyst from a) monopodal and b) bipodal bis oxo molybdenum surface species

Although recent attempts were aimed at the establishment of a structure-reactivity directly on conventional metathesis catalysts by advanced in-operando spectroscopies (Raman, EXAFS) under a flow of propene, the nature of the active sites remains a matter of debate. The challenge lies on the heterogeneity of these systems where only few percent of the metal loading is active, which precludes precise characterization of the desired site. Therefore, the selective preparation of well-defined, single-site oxo carbene molybdenum surface species may bring valuable information on the activation mechanism and the nature of the active sites. The surface organometallic chemistry (SOMC), which consists in the grafting of organometallic precursor by protonolysis with remaining surface OH groups of a partially dehydroxylated oxide surface (□AlOH, □SiOH…), has proved to be a powerful tool to prepare well-defined surface species.[10,11] Despite the demonstrated effectiveness of supported MoO_3 catalyst, no real well-defined surface species bearing an oxo carbene that could serve as a model has been prepared yet. Instead, tremendous amounts of works have focused on their imido analogues though the grafting of Schrock's complexes onto silica partially dehydroxylated at 700 °C, which usually only gives monopodal surface species.[12] This led to an increase of the initial activity by tuning of the σ-donor pendant ligand, but inevitably led to catalyst showing fast deactivation. Besides, we have pioneered the preparation of well-defined tungsten oxo alkyl species supported onto silica such as $(\square SiO\text{-})WO(CH_2{}^{t}Bu)_3$ or $(\square SiO)_2WO(CH_2SiMe_3)_2$ that serve as realistic model of the active species of the WO_3/SiO_2 olefin metathesis catalyst.[13,14,15,16,17,18] With these surface species prompt to carbene formation by α-H abstraction we have found that switching the ancillary ligand from an imido to an oxo drastically increases the activity and stability of the catalyst.

We intent to access monopodal active species by preparing a monosiloxy molybdenum oxo carbene surface species by SOMC in order to compare its activity and deactivation process with the industrial catalyst MoO_3/SiO_2. The issue here is clearly the availability of suitable starting organometallic complexes, as such compounds are notoriously difficult to access. Nevertheless, up to now, only one example of molecular molybdenum oxo carbene complex bearing bulky phosphinimide ligands has been reported.[19] This complex is inactive in olefin metathesis due to the low electrophilicity of the metal center and the extreme bulkiness of the ancillary ligands. Therefore, we turned our attention to the grafting of alkyl species amenable to carbene formation by α-H abstraction. Osborn et al. described the preparation of $MoO(CH_2{}^{t}Bu)_3Cl$, which is an active olefin metathesis catalyst in the presence of a Lewis acid.[20] Herein, we report the grafting of $MoO(CH_2{}^{t}Bu)_3Cl$ (**1**) on dehydroxylated silica at 700 °C to yield the targeted monopodal surface species. This new material has been fully characterized, and its catalytic performances in propene self-metathesis were investigated and compared to the supported molybdenum imido counterparts, as well as its tungsten oxo analogue.



Scheme 2. Reaction of **1** with **$SiO_{2\text{-}700}$**

We studied the grafting of **1** onto silica partially dehydroxylated at 700 °C ($SiO_{2\text{-}700}$) bearing only isolated silanols at room temperature without solvent. During the grafting on silica, the reaction can occur either by protonolyis of Mo-Cl or Mo-C bonds (Scheme 2). As reported for the analogue tungsten oxo complex, the grafting reaction is performed under dynamic vacuum to remove the HCl potentially formed in order to shift the equilibrium toward the grafting of the complex. The DRIFT spectrum (Figure 1) shows the almost complete consumption of the free silanols at 3747 cm^{-1} and the concomitant appearance of CH stretching bands spanning from 2850 to 3030 cm^{-1}. Furthermore the elemental analysis gives a Mo and carbon loading of 2.05 $_{wt}$% and 4.09 $_{wt}$% respectively, which correspond to a C/Mo ratio of 15.9 and a Mo/Silanol ratio of 0.98. The gas phase analysis of the grafting performed under vacuum reveal the release of only traces of neopentane and quantification of the HCl released by IR shows the released of ca 0.85 HCl per molybdenum.

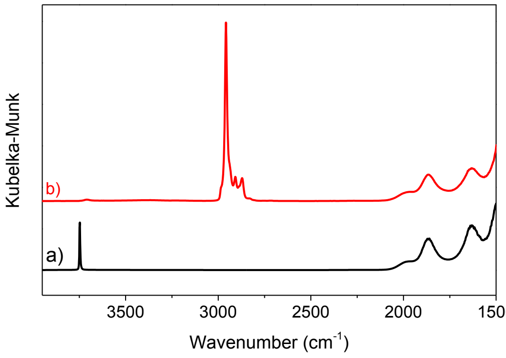


Figure 1. DRIFT spectra of $SiO_{2\text{-}700}$ (a), grafted **$1/SiO_{2\text{-}700}$** (b)

In addition ^1H MAS and ^{13}C CPMAS spectra along with ^1H-^{13}C HETCOR correlation experiment (Figure 2) reveal the presence of methylenic fragment at 2.7 and 86.8 ppm (in ^1H and ^{13}C NMR, respectively) along with methyl resonances at 1.2 (^1H) and 30.7 (^{13}C) ppm. The ^{13}C CPMAS also features a signal at 34.9 ppm that does not correlate on the HETCOR spectrum, in line with its assignement as quaternary carbons of the neopentyl ligands. Thus, these elements are in line with the formation of the monopodal $(\square SiO)MoO(CH_2{}^{t}Bu)_3$ as the major surface species. The same reactivity has already been observed for the related tungsten oxo species $WO(CH_2{}^{t}Bu)_3Cl$.[13] Thus, the selectivity of the silanolysis of the M-C vs. the M-Cl bond is similar for both metals.

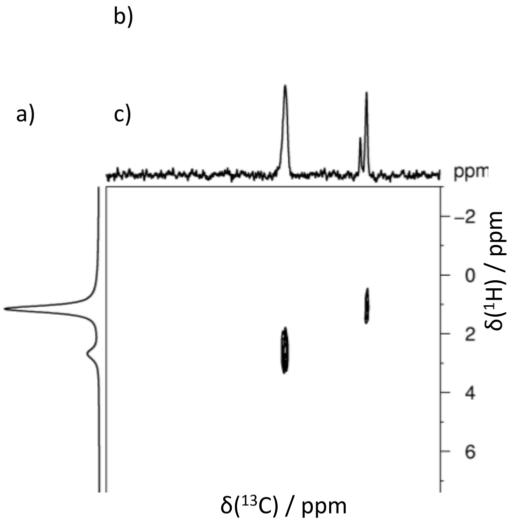


Figure 2. (a) ^1H MAS, (b) ^{13}C CP and (c) ^1H-^{13}C CP-HETCOR MAS NMR spectra of **$1/SiO_{2\text{-}700}$** (11.75 T, spinning speed 10 kHz).

The structure of the supported complex **$1/SiO_{2\text{-}700}$**, resulting from the reaction of $Mo(O)Cl(Np)_3$ with $SiO_{2\text{-}700}$, was also studied by EXAFS (Figure S1 and Table 1). The results are consistent with the following coordination sphere around Mo: (i) one oxo ligand at 1.689(5) Å, (ii) one oxygen at 2.00(2) Å, which can be assigned to a surface siloxide ligand and (iii) three carbon atoms at 2.13(1) Å, attributed to three neopentyl ligands. The lengths found for Mo-O and Mo-C single-bonds are in good agreement with those observed by XRD for molecular complexes as [Mo(CH$_2$CMe$_2$Ph)$_3$(=N-NPh$_2$)(OC$_6$F$_5$)] (2.011(2) Å for Mo-O and 2.123 to 2.155 Å for Mo-C)[21] or [(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{12}$SiO-Mo(=NH)(CH$_2$CMe$_3$)$_3$] (1.984(2) Å for Mo-O and 2.116 to 2.126 Å for Mo-C),[22] while the length found for the Mo=O bond lies within the usually observed range, for instance 1.699(3) Å for [Cp*Mo(=O)(CH$_2$CMe$_3$)(2,2-dimethylpropylnitrosyl)] (2.204(4) Å for Mo-C)[23] and between 1.703 and 1.712 Å for [Mo(=O)$_2$(CH$_2$CMe$_3$)$_2$(2,2'-bipyridyl)][24] (2.230 to 2.242 Å for Mo-C). Similar parameters were obtained when fitting the k^2.χ(k) spectrum. The fit could be improved by adding a layer of further backscatterers, three carbon and one silicon atoms at 3.26(3) and 3.64(5) Å respectively, attributed to the quaternary carbon of the neopentyl and to the silicon of the surface siloxide ligands and one oxygen at 2.80(4) which can be attributed to a surface oxygen from a siloxane bridge of the silica support. This EXAFS study fully agrees with the monopodal structure □SiO-Mo(O)(Np)$_3$ for the silica supported complex **1/SiO$_{2\text{-}700}$**.

Table 1. EXAFS parameters for the supported complex 1/SiO$_{2\text{-}700}$.[a]

Type of neighbor	Number of neighbors	Distance (Å)	σ^2 (Å^2)
Mo=***O***	1	1.689(5)	0.0016(4)
Mo-***O***	1	2.00(2)	0.0025(11)
Mo-***C***H$_2$CMe$_3$	3	2.13(1)	0.0033(5)
Mo--O(***Si***≡)$_2$	1	2.80(4)	0.009(5)
Mo-CH$_2$***C***Me$_3$	3	3.26(3)	0.0066(33)
Mo--***Si***≡ [b]	1	3.64(5)	0.025(8)

The errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. [a] Δk: [2.6-16.9 Å^{-1}] - ΔR: [0.7-3.4 Å] ([0.8-2.2 Å], when considering only the first coordination sphere); $S_0^2 = 0.96$; $\Delta E_0 = 4.0 \pm 1.4$ eV (the same for all shells); Fit residue: ρ = 3.2 %; Quality factor: $(\Delta\chi)^2/\nu = 3.46$, with $\nu = 13 / 27$ ($[(\Delta\chi)^2/\nu]_1 = 3.99$ with $\nu = 15/22$, considering only the first coordination sphere: =O, -O and -C). [b] Two multiple scattering pathways have also been considered in the fit but not mentioned in this table.

The catalytic performances of **1/SiO$_{2\text{-}700}$** in propylene self-metathesis were probed in a flow reactor (40 ml$_{C3H6}$ min^{-1}; 30 °C; 290 mol$_{C3H6}$ mol$_{Mo}^{-1}$ min^{-1}). A maximum conversion of about 36.4 %, just below the thermodynamic equilibrium, is rapidly reached. Then, the catalyst deactivates before reaching a pseudo plateau at about 17 % conversion, leading to an outstanding TON of 89200 after 25 h. Interestingly, under these conditions the catalyst does not show any activation period contrary to that previously observed for the tungsten analogues.[13,18] The selectivity in metathesis products (ethylene, 2-butenes) remains constant with time on stream with no other higher olefin detected (Figure S2). The trans/cis-2-butene ratio (Thermodynamic ratio 3.1) evolves with time on stream from 2.8 to 1.6 following the decrease of activity due to a decrease of *cis/trans* isomerization rate achieved by degenerated olefin metathesis (Scheme S1).[25] Noteworthy, contrary to the related molecular precatalyst MoO(CH$_2{}^t$Bu)$_3$Cl, the supported surface species does not require the addition of a Lewis acid to display high activity in olefin metathesis.

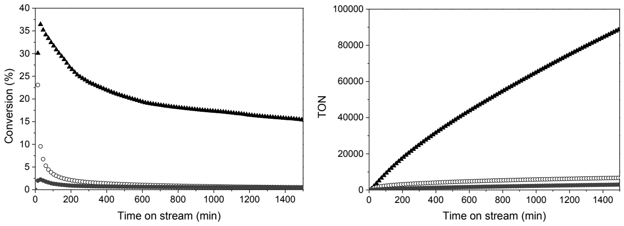


Figure 3. Conversion (a) and cumulated TON (b) of propylene self metathesis (40 mL of C$_3$H$_6$ min^{-1}; 30 °C; 290 mol of C$_3$H$_6$ (mol of Mo)$^{-1}$ min^{-1}, 1 bar) over **1/SiO$_{2\text{-}700}$** (□), **2/SiO$_{2\text{-}700}$** (□) and (□SiO)WO(CH$_2{}^t$Bu)$_3$ **3/SiO$_{2\text{-}700}$** (□).

We then compared this catalyst with supported monopodal imido surface complexes that have been described in the literature to be more active than classical heterogenous molybdenum-based catalysts. Despite a high initial turn-over frequency (TOF) of 26.2, (□SiO)Mo(=NAr)(=CH^{t}Bu)(CH$_2{}^t$Bu), (**2/SiO$_{2\text{-}700}$**) rapidly deactivates to give a conversion of only ca. 0.7 % at the pseudo-plateau, which corresponds to a moderate TON of 6710 after 25 h. The only products observed (Figure S3) are ethylene and butenes showing a high selectivity in metathesis. At low conversion, the *cis* product is the major butene isomer at the pseudo plateau. Isobutene is observed in trace amount with a selectivity curve that parallel that of the deactivation curve, suggesting a similar deactivation pathway than the tungsten analogue.[13] This result shows that the switch from a imido ancillary ligand to an oxo is beneficial for the overall activity of the catalyst. We have also compared the catalyst **1/SiO$_{2\text{-}700}$** to its tungsten analogue (□SiO)WO(CH$_2{}^t$Bu)$_3$ **3/SiO$_{2\text{-}700}$.** This later has shown a respectable and sustained activity in propene self-metathesis at 80 °C with a flow rate of 20 ml min^{-1} reaching a TON of about 6000 after 25h (Table 2).[13] At room temperature **3/SiO$_{2\text{-}700}$** is less active, exhibiting a conversion of 2 % which decreases to 0.6 % at the pseudo plateau with a TON of 2960 after 25 h. Indeed, **1/SiO$_{2\text{-}700}$** (TOF$_{\text{initial}}$ = 102.1) shows a much higher initial catalytic activity than **3/SiO$_{2\text{-}700}$** (TOF$_{\text{initial}}$ = 5.6), suggesting that activation of the molybdenum pre-catalyst is more facile.[3] Finally, we intended to compare our new catalyst to MoO$_3$/SiO$_2$ prepared by classical method and activated at 550 °C under propylene (according to Stair et al.'s procedure). However, MoO$_3$/SiO$_2$ displays a low activity in propene self-metathesis with a TON of 250 at 25 h under our conditions. Nevertheless, if one takes into account that less than 5% of the molybdenum centers are active,[4,26] the catalytic activity (TOF) of MoO$_3$/SiO$_2$ becomes comparable to that of **1/SiO$_{2\text{-}700}$,** which validates our structure hypothesis for the active species of the industrial catalyst. Thus, the current study demonstrates the importance for surface organometallic chemistry to access well-defined surface species which has in this case shown a large improvement on the catalytic activity under very mild operating conditions.

Table 2. Comparative Propylene Metathesis Results for the Molybdenum Catalysts: Activity (Cumulated TON) and Product Selectivity after 25 h of Reaction in a Dynamic Flow Reactor at 30 °C.

Precatalyst	TOF[a]	TON[b]	Product selectivity [%][c]			
	at (60 min)	(after 25 h)	ethylene	*E*-2-butene	*Z*-2-butene	*Z*/*E*
$(\square SiO)MoO(CH_2{}^tBu)_3$ $\mathbf{1/SiO_{2\text{-}700}}$	102.1	89260	50.0	30.9	19.1	0.62
$(\square SiO)Mo(=NAr)(=CH{}^tBu)(CH_2{}^tBu)$ $\mathbf{2/SiO_{2\text{-}700}}$	26.2	6710	50.0	21.4	28.6	1.33
$(\square SiO)WO(CH_2{}^tBu)_3$ $\mathbf{3/SiO_{2\text{-}700}}$	5.6	2960	50.0	23.1	26.9	1.16
$(\square SiO)WO(CH_2{}^tBu)_3$ $\mathbf{3/SiO_{2\text{-}700}}$ [d]	4.9	6000	50.0	32.3	17.7	0.55
MoO_3/SiO_2[e]	0.5	250	50.0	25.4	24.6	0.96

[a]TOF is expressed in mol of propylene transformed/mol of metal/min. [b]TON is expressed in mol of propylene transformed/mol of metal. [c]Selectivities are defined as the molar amount of product over the total molar amount of products, at the end of the reaction (1500 min). [d]reaction performed at 80 °C, 20 ml min^{-1}, ($R = 60\ mol_{C3H6}\ mol_{Mo}{}^{-1}\ min^{-1}$). [e] reaction performed at 30 °C, 10 ml/min ($R = 17.5\ mol_{C3H6}\ mol_{Mo}{}^{-1}\ min^{-1}$)

In conclusion, we have prepared and characterized the first example of well-defined molybdenum oxo alkyl species, precursor to highly active olefin metathesis catalyst performing at low temperature (30 °C). This catalyst outperforms its tungsten and imido counterparts by an order of magnitude. The preparation of well-defined surface single site species via SOMC leads to an increase of activity much higher than the heterogeous MoO_3/SiO_2 system (TON after 25 h, 89200 vs 250), which is known to bear different surface species and for which only few percent of the metal sites are active.[26] This is a further step forward the understanding of the nature of the active site of industrial MoO_3/SiO_2 olefin metathesis catalysts that can pave the way to the preparation of highly active systems. In a further step we aim to access to bipodal surface species, the second reported putative active species in supported industrial MoO_3 system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures
Molybdenum K-edge k^3-weighted EXAFS
Molar selectivities.

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Notes

The authors declare no competing financial interests.

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