

Well-Defined Molybdenum Oxo Alkyl Complex Supported on Silica by Surface Organometallic Chemistry: A Highly Active Olefin Metathesis Precatalyst

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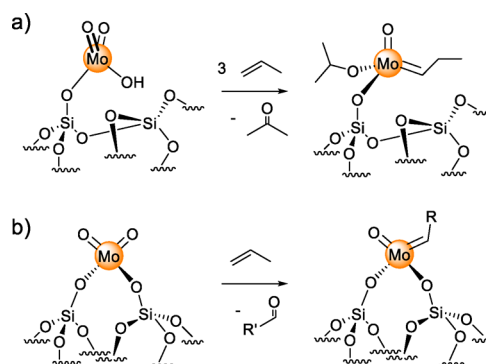
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Supporting Information

ABSTRACT: The well-defined silica-supported molybdenum oxo alkyl species ($\equiv\text{SiO}-$) $\text{MoO}(\text{CH}_2^t\text{Bu})_3$ was selectively prepared by grafting of $\text{MoO}(\text{CH}_2^t\text{Bu})_3\text{Cl}$ onto partially dehydroxylated silica (silica₇₀₀) using the surface organometallic chemistry approach. This surface species was fully characterized by elemental analysis and DRIFT, solid-state NMR, and EXAFS spectroscopy. This new material is related to the active species of industrial supported $\text{MoO}_3/\text{SiO}_2$ olefin metathesis catalysts. It displays very high activity in propene self-metathesis at mild (turnover number = 90 000 after 25 h). Remarkably, its catalytic performance outpaces those of the parent imido derivative and 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} olefins using the Shell higher olefin process.¹ The latter 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 types of surface metallic species (monomeric, oligomeric, and clustered molybdates), leading to the proposal of several activation pathways from monopodal or bipodal surface species.^{4–6} Trunschke and co-workers suggested, on the basis of IR and 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 that in the presence of propylene gives a monopodal isopropoxyl molybdenum oxo carbene with concomitant release of an acetone molecule (Scheme 1a).⁴ However, the actual active

Scheme 1. Proposed Active Species of Industrial Mo Catalyst from (a) Monopodal and (b) Bipodal Bis(oxo) Molybdenum Surface Species



species has also been stated to be an isolated bipodal molybdenum oxo carbene surface species.^{3,5,7} Recent works from Stair and co-workers 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 (Scheme 1b).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 restructuring, 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}

Although recent attempts were aimed at establishing a structure–reactivity relationship directly on conventional metathesis catalysts by advanced in operando spectroscopies (Raman, EXAFS) under a flow of propene, the nature of the active sites

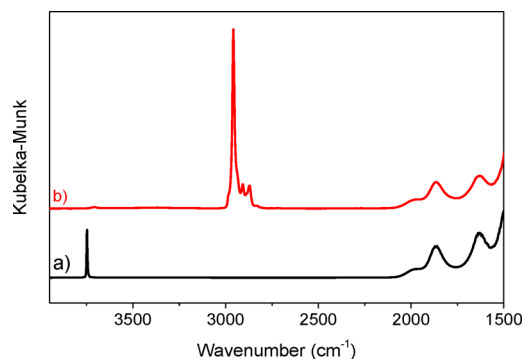
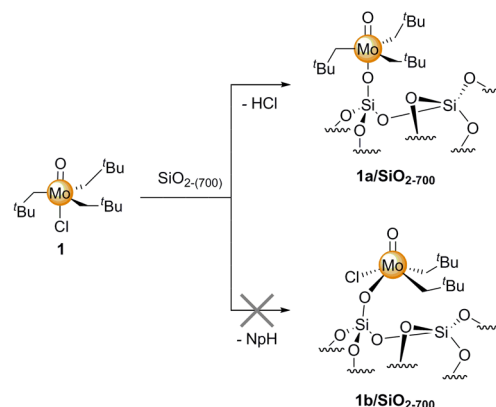
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remains a matter of debate. The challenge lies in the heterogeneity of these systems, where only few percent of the metal loading is active, which precludes precise characterization of the desired site. Therefore, the selective preparation of well-defined, single-site oxo carbene molybdenum surface species may provide valuable information about the activation mechanism and the nature of the active sites. The surface organometallic chemistry (SOMC) approach, which consists of grafting an organometallic precursor by protonolysis with remaining surface OH groups of a partially dehydroxylated oxide surface ($\equiv\text{AlOH}$, $\equiv\text{SiOH}$, etc.), has proved to be a powerful tool to prepare well-defined surface species.^{10,11} Despite the demonstrated effectiveness of the supported MoO_3 catalyst, no real well-defined surface species bearing an oxo carbene that could serve as a model has been prepared to date. Instead, tremendous amounts of work have focused on their imido analogues though the grafting of Schrock's complexes onto silica that was partially dehydroxylated at 700 °C, which usually only gives monopodal surface species.¹² This led to an increase in the initial activity by tuning of the σ -donor pendant ligand but inevitably led to fast deactivation of the catalyst. Besides, we have pioneered the preparation of well-defined tungsten oxo alkyl species supported on silica, such as $(\equiv\text{SiO}-)\text{WO}(\text{CH}_2^t\text{Bu})_3$ and $(\equiv\text{SiO})_2\text{WO}(\text{CH}_2\text{SiMe}_3)_2$, that serve as realistic models of the active species of the WO_3/SiO_2 olefin metathesis catalyst.^{13–18} With these surface species tendency to form carbenes 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.

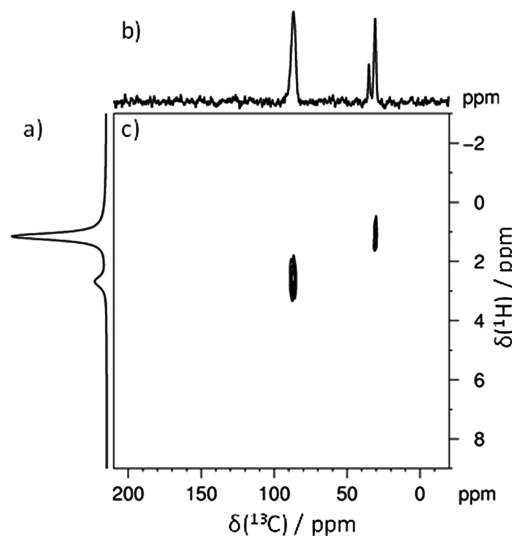
We aimed to access a monopodal active species by preparing a monosiloxy molybdenum oxo carbene surface species by SOMC in order to compare its activity and deactivation process with those of the industrial catalyst $\text{MoO}_3/\text{SiO}_2$. The issue here is clearly the availability of suitable starting organometallic complexes, as such compounds are notoriously difficult to access. Nevertheless, to date only one example of a molecular molybdenum oxo carbene complex bearing bulky phosphinimide ligands has been reported.¹⁹ This complex is inactive in olefin metathesis because of 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 and co-workers described the preparation of $\text{MoO}(\text{CH}_2^t\text{Bu})_3\text{Cl}$ (**1**), which is an active olefin metathesis catalyst in the presence of a Lewis acid.²⁰ Herein we report the grafting of **1** onto dehydroxylated silica at 700 °C to yield the targeted monopodal surface species. This new material has been fully characterized, and its catalytic performance in propene self-metathesis was investigated and compared with those of the supported molybdenum imido counterparts as well as its tungsten oxo analogue.

We studied the grafting of **1** onto silica that was partially dehydroxylated at 700 °C and contained only isolated silanols at room temperature ($\text{SiO}_{2-(700)}$) without solvent. During the grafting on silica, the reaction can occur by protonolysis of either the Mo–Cl or Mo–C bond (Scheme 2). As reported for the analogous tungsten oxo complex, the grafting reaction was 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 gave Mo and carbon loadings of 2.05 and 4.09 wt %, respectively,

Scheme 2. Reaction of **1** with SiO_{2-700} Figure 1. DRIFT spectra of (a) SiO_{2-700} and (b) grafted **1**/ SiO_{2-700} .

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 revealed the release of only traces of neopentane (NpH), and quantification of the HCl released by IR spectroscopy showed a release of ca. 0.85 HCl per Mo.

In addition, ^1H MAS and ^{13}C CPMAS spectra along with a ^1H – ^{13}C HETCOR correlation experiment (Figure 2) revealed the presence of the methylenic fragment at 2.7 ppm (^1H) and 86.8 ppm (^{13}C) along with methyl resonances at 1.2 ppm (^1H)

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

and 30.7 ppm (^{13}C). The ^{13}C CPMAS spectrum also features a signal at 34.9 ppm that does not correlate on the HETCOR spectrum, in line with its assignment as quaternary carbons of the neopentyl ligands. Thus, these elements are in line with the formation of monopodal ($\equiv\text{SiO}$)MoO(CH $_2^t$ Bu) $_3$ as the major surface species. The same reactivity was observed previously for the related tungsten oxo species WO(CH $_2^t$ Bu) $_3$ Cl.¹³ Thus, the selectivity for the silanolsysis of the M–Cl bond versus the M–C bond is similar for the two metals.

The structure of the supported complex **1**/SiO $_{2-700}$ resulting from the reaction of Mo(O)Cl(Np) $_3$ with SiO $_{2-700}$ was also studied by EXAFS (Figure S1 and Table 1). The results are

Table 1. EXAFS Parameters for the Supported Complex **1**/SiO $_{2-700}$ ^a

type of neighbor	number of neighbors	distance (Å) ^b	σ^2 (Å 2) ^b
Mo=O	1	1.689(5)	0.0016(4)
Mo–O	1	2.00(2)	0.0025(11)
Mo–CH $_2$ CMe $_3$	3	2.13(1)	0.0033(5)
Mo...O(Si \equiv) $_2$	1	2.80(4)	0.009(5)
Mo–CH $_2$ CMe $_3$	3	3.26(3)	0.0066(33)
Mo...Si \equiv ^c	1	3.64(5)	0.025(8)

^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: $\rho = 3.2\%$; 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). ^bThe errors generated by the EXAFS fitting program “RoundMidnight” are indicated in parentheses. ^cTwo multiple scattering pathways were also considered in the fit but are not mentioned in this table.

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 Np ligands. The lengths found for the Mo–O and Mo–C single bonds are in good agreement with those observed by XRD for molecular complexes such as [Mo(CH $_2$ CMe $_2$ Ph) $_3$ (=N–NPh $_2$)(OC $_6$ F $_5$)] (2.011(2) Å for Mo–O and 2.123–2.155 Å for Mo–C)²¹ and [(*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 2.116–2.126 Å for Mo–C),²² while the length found for the Mo=O bond lies within the usually observed range, e.g., 1.699(3) Å for [Cp*Mo(=O)(CH $_2$ CMe $_3$) $_2$ (2,2-dimethylpropylnitrosyl)] (2.204(4) Å for Mo–C)²³ and 1.703–1.712 Å for [Mo(=O) $_2$ (CH $_2$ CMe $_3$) $_2$ (2,2'-bipyridyl)]²⁴ (2.230–2.242 Å for Mo–C). Similar parameters were obtained from fitting of the $k^2\chi(k)$ spectrum. The fit could be improved by adding a layer of further backscatterers, three carbon atoms and one silicon atom at 3.26(3) and 3.64(5) Å, respectively, attributed to the quaternary carbons of the neopentyl groups and the silicon of the surface siloxide ligand, and one oxygen at 2.80(4) that can be attributed to a surface oxygen from a siloxane bridge of the silica support. This EXAFS study fully agrees with the monopodal structure $\equiv\text{SiO}$ –Mo(O)(Np) $_3$ for the silica-supported complex **1**/SiO $_{2-700}$.

The catalytic performances of **1**/SiO $_{2-700}$ in propylene self-metathesis were probed in a flow reactor (40 mL C $_3$ H $_6$ min $^{-1}$; 60 °C; 290 mol C $_3$ H $_6$ mol Mo $^{-1}$ min $^{-1}$). A maximum conversion of about 36.4%, just below the thermodynamic equilibrium, was rapidly reached (Figure 3). Then the catalyst deactivated before reaching a pseudoplateau at about 17% conversion, leading to an

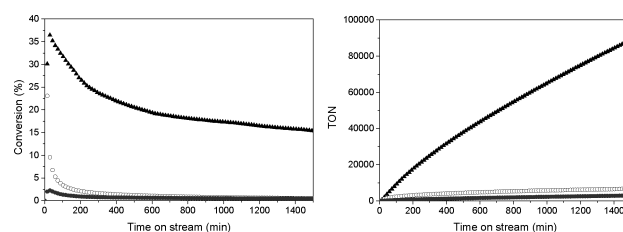


Figure 3. (a) Conversion and (b) cumulative TON of propylene self-metathesis (40 mL C $_3$ H $_6$ min $^{-1}$; 60 °C; 290 mol C $_3$ H $_6$ mol Mo $^{-1}$ min $^{-1}$, 1 bar) over **1**/SiO $_{2-700}$ (\blacktriangle), **2**/SiO $_{2-700}$ (\circ), and ($\equiv\text{SiO}$)WO(CH $_2^t$ Bu) $_3$ (**3**/SiO $_{2-700}$) (\bullet).

outstanding turnover number (TON) of 89 200 after 25 h. Interestingly, under these conditions the catalyst did not show any activation period, contrary to that previously observed for the tungsten analogues.^{13,18} The selectivity in metathesis products (ethylene, 2-butenes) remained constant with time on stream, with no other higher olefin detected (Figure S2). The *trans*/*cis*-2-butene ratio (thermodynamic ratio 2.8) evolved with time on stream from 2.8 to 1.6, following the decrease in activity due to a decrease in the *cis*/*trans* isomerization rate achieved by degenerate olefin metathesis (Scheme S1).²⁵ It is noteworthy that 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.

We then compared this catalyst with supported monopodal imido surface complexes that have been described in the literature as more active than classical heterogeneous Mo-based catalysts. Despite a high initial turnover frequency (TOF) of 26.2, ($\equiv\text{SiO}$)Mo(=NAr)(=CH t Bu)(CH $_2^t$ Bu) (**2**/SiO $_{2-700}$) rapidly deactivated to give a conversion of only ca. 0.7% at the pseudoplateau, which corresponds to a moderate TON of 6710 after 25 h. The only products observed (Figure S3) were ethylene and butenes, showing a high selectivity in metathesis. At low conversion, the *cis* product was the major butene isomer at the pseudoplateau. Isobutene was observed in trace amount with a selectivity curve paralleling the deactivation curve, suggesting a similar deactivation pathway as for the tungsten analogue.¹³ This result shows that the switch from an imido ancillary ligand to an oxo ligand is beneficial for the overall activity of the catalyst. We also compared **1**/SiO $_{2-700}$ to its tungsten analogue ($\equiv\text{SiO}$)WO(CH $_2^t$ Bu) $_3$ (**3**/SiO $_{2-700}$), which showed 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 25 h (Table 2).¹³ At 60 °C **3**/SiO $_{2-700}$ is less active, exhibiting a conversion of 2% that decreases to 0.6% at the pseudoplateau with a TON of 2960 after 25 h. Indeed, **1**/SiO $_{2-700}$ (TOF $_{\text{initial}} = 102.1$) shows a much higher initial catalytic activity than **3**/SiO $_{2-700}$ (TOF $_{\text{initial}} = 5.6$), suggesting that activation of the molybdenum precatalyst is more facile.³ Finally, we intended to compare our new catalyst to MoO $_3$ /SiO $_2$ prepared by the classical method and activated at 550 °C under propylene (according to the procedure of Stair and co-workers). 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 $_{2-700}$, which validates our structure hypothesis for the active species of the industrial catalyst. Thus, the current study demonstrates the importance of SOMC to access well-defined surface species, which has in this

Table 2. Comparative Propylene Metathesis Results for the Molybdenum Catalysts: Activity (Cumulative TON) and Product Selectivity after 25 h of Reaction in a Dynamic Flow Reactor at 60 °C

precatalyst	TOF _{60 min} ^a	TON _{25 h} ^b	product selectivity [%] ^c			
			ethylene	(E)-2-butene	(Z)-2-butene	Z/E
1/SiO ₂₋₇₀₀	102.1	89260	50.0	30.9	19.1	0.62
2/SiO ₂₋₇₀₀	26.2	6710	50.0	21.4	28.6	1.33
3/SiO ₂₋₇₀₀	5.6	2960	50.0	23.1	26.9	1.16
3/SiO ₂₋₇₀₀ ^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

^aTOF is expressed in moles of propylene transformed per mole of metal per minute. ^bTON is expressed in moles of propylene transformed per mole of metal. ^cSelectivity is defined as the molar amount of product over the total molar amount of all products at the end of the reaction (1500 min).

^dThe reaction was performed at 80 °C and 20 mL min⁻¹, ($R = 60 \text{ mol}_{\text{C}_3\text{H}_6} \text{ mol}_{\text{Mo}}^{-1} \text{ min}^{-1}$). ^eThe reaction was performed at 60 °C and 10 mL/min ($R = 17.5 \text{ mol}_{\text{C}_3\text{H}_6} \text{ mol}_{\text{Mo}}^{-1} \text{ min}^{-1}$)

case shown a large improvement in the catalytic activity under very mild operating conditions.

In conclusion, we have prepared and characterized the first example of a well-defined molybdenum oxo alkyl species as a precursor to a highly active olefin metathesis catalyst performing at low temperature (60 °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 in activity to a value that is much higher than that of the heterogeneous MoO₃/SiO₂ system (TON after 25 h: 89 200 vs 250), which is known to bear different surface species and for which only a few percent of the metal sites are active.²⁶ This is a further step forward in understanding the nature of the active site of industrial MoO₃/SiO₂ olefin metathesis catalysts that can pave the way to the preparation of highly active systems. In a further step, we aim to access to a bipodal surface species, the second reported putative active species in the supported industrial MoO₃ system.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11220.

Procedures and additional data (PDF)

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Notes

The authors declare no competing financial interest.

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