Silica-Supported Isolated Molybdenum Di-oxo Species: Formation and Activation with Organosilicon Agent for Olefin Metathesis

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A well-defined silica-supported molybdenum dioxo species, $(\equiv\text{SiO})_2\text{Mo}(\text{O})_2$, is prepared by grafting $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ on partially dehydroxylated silica SiO_{2-700} , followed by thermal treatment under high-vacuum and calcination. Activated by an organosilicon agent the resulting catalysts is active for olefin metathesis at 30 °C.

Olefin metathesis is a widely used reaction to efficiently build C=C double bonds of organic molecules, with applications ranging from the synthesis of basic chemicals to complex molecular architectures and polymers.^{1, 2} Among transition metal based olefin metathesis catalysts, molybdenum catalysts are particularly active and are mostly based on high oxidation state Mo(VI) species whether looking at well-defined Mo alkylidene complexes³⁻⁵ or catalysts based on supported Mo oxides.⁶ The latter have been continuously used in industrial petrochemical processes since their discovery in the 1960's, in particular in the Shell Higher Olefin Process (SHOP), which produces long-chained olefins (up to C₂₀) from ethylene.⁷ ⁸ Large research efforts have been devoted to increase the activity and the number of active sites.⁹⁻¹² However, the variety of metal sites, such as monomeric MoO_x, oligomeric MoO_x, and crystalline MoO_x NPs¹³⁻¹⁸ makes it particularly challenging to elaborate simple and efficient strategies to tune the activation steps and the resulting catalytic efficiency of these systems.

Figure 1. A) The representative view of the way to generate metal oxide sites by means of combined SOMC and TMP approaches. Subscripts, m, n, p, and q represent the number of the ligands. $M(O)_n[OSi(OtBu)_3]_m$ are ideal molecular complexes because $OSi(OtBu)_3$ ligand can convert into other siloxide or oxo ligands around metal center through thermal decomposition. B) Prepared W (**3**) and Mo (**2**) oxo species on silica surface by SOMC and TMP approaches. C) Reduction of metal oxo sites by Me_4BTDP .

Here, we report the selective generation of molecularly-defined $(\equiv SiO)_2Mo(O)_2$ by using Surface Organometallic Chemistry (SOMC)¹⁹⁻²² combined with the Thermolytic Molecular Precursor (TMP) approach,^{23, 24} which has been used to generate isolated metal ions including tungsten oxo species on silica (Figures 1A, 1B).^{20, 21, 25, 26} We show that this approach provides access to well-defined molybdenum di-oxo species, which are highly active in olefin metathesis upon activation by organosilicon agents, 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (Me_4BTDP) (Figure 1C).²⁷

Figure 2. Synthesis and characterization of **2**. (A) Grafting of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ on SiO_{2-700} to give **1** including the site $(\equiv\text{SiO})\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]$, followed by thermal treatment and calcination to yield **2** including the site $(\equiv\text{SiO})_2\text{Mo}(\text{O})_2$. (B) XANES spectra of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$, **1**, and **2**. (C) The fit of the EXAFS spectrum of **1** in *k*-space (top plot) and *R*-space (bottom plot). (D) The fit of the EXAFS spectrum of **2** in *k*-space (top plot) and *R*-space (bottom plot).

First, the molecular precursor complex, $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ (the crystal structure is shown in Figure S1),²⁸ is reacted at room temperature with a partially dehydroxylated silica (SiO_{2-700} , 0.95 equiv. of SiOH to Mo) in benzene/dimethoxyethane ($v:v = 100:5$) to give a white solid **1** (Figure 2A). During the process, 0.54 equiv. of $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ is consumed, while 0.42 equiv. of $\text{HOSi}(\text{OtBu})_3$ is released, thus indicating grafting of the molecular precursor. The IR measurement of **1** shows the disappearance of isolated SiOH (3746 cm^{-1}) and the appearance of the C-H stretching signals between $2800\text{--}3050\text{ cm}^{-1}$ and a broad silanol band centered at 3364 cm^{-1} consistent with the presence of the organic ligand interacting with the residual surface silanols (Figure S2). The material **1** is heated at 200 °C for 3 h, then 400 °C for 8 h under 10^{-5} mbar followed by a calcination step at 400 °C to generate isolated $\text{Mo}(\text{VI})$ surface species (*vide infra*).[§] During the thermal treatment under vacuum, the $\text{OSi}(\text{OtBu})_3$ ligand decomposes into isobutene and *tert*-butanol, which can be detected by ^1H NMR measurement. The IR spectrum of **2** shows no absorption bands associated with organic ligands, demonstrating their full removal under these conditions (Figure S2). Elemental analysis of the material **2** shows a molybdenum content of 1.56%_{wt}

(0.163 mmol Mo/g), which corresponds to a site density of ca. 0.5 Mo/nm², analogous to that found for its tungsten analogue **3** (Figure 1B, 0.5 W/nm²).²⁵

UV-vis diffuse reflectance spectra (UV-vis-DRS) of the material **1** and **2** under inert condition show strong absorption in a range 200–400 nm due to the ligand to metal charge transfer (LMCT) transitions associated with an electronic edge energy (E_g) of 3.7 and 3.9 eV, respectively (Figures S7, S8). This is slightly lower than that of Mo(O)₂[OSi(OtBu)₃]₂ (4.0 eV, Figure S6), which likely results from the more distorted monomolybdenate structure of the surface species present in **1** and **2**.²⁹⁻³¹

To obtain further information on the structure of Mo species, measurements of Mo K-edge X-ray absorption spectroscopy (XAS) were conducted. An identical Mo K-edge X-ray absorption near edge structure (XANES) edge energy of 20014.9 eV was measured for **1**, **2**, and Mo(O)₂[OSi(OtBu)₃]₂, leading to the assignment of **1** and **2** as Mo(VI) species (Figure 2B). Additionally, a similar high intensity of pre-edge feature is observed for Mo(O)₂[OSi(OtBu)₃]₂ and **2**, in agreement with a tetrahedral geometry for both compounds. Noticeably, **1** shows a smaller pre-edge peak compared to **2**, which indicates that the molybdenum centers in **1** are slightly more centro symmetrical, presumably due to the additional interactions with siloxane bridges on the silica surface. Extended X-ray absorption fine structure (EXAFS) analysis of **1** indicates that the molybdenum center is coordinated by two oxygen atoms 1.723(5) Å and two oxygen atoms at 1.952(7) Å, consistent with the formation of (≡SiO)Mo(O)₂[OSi(OtBu)₃] species (Figure 2C and Table S4). The fit also improves significantly by including an additional Mo-O scattering path at 2.39(2) Å, suggesting the presence of an interaction with a surface siloxane bridge. EXAFS analysis of **2** analogously shows two O neighbors at 1.699(5) Å and two O neighbors at 1.921(6) Å, indicating the formation of (≡SiO)₂Mo(O)₂ as a major molybdenum site in **2** (Figure 2D). These isolated tetrahedral Mo dioxo centers are in fact similar to those observed in supported Mo systems prepared by impregnation at low loading.³²⁻³⁵ However, these results on Mo contrasts with what is observed for the tungsten analogue **3**, constituted by a 1:1 mixture of (≡SiO)₂W(O)₂ and (≡SiO)₄W(O) species (Figure

1B).²⁵ Furthermore, no Mo-Mo scattering path is observed in both **1** and **2**, suggesting the presence of isolated Mo sites.

Figure 3. Conversion vs time, *cis*-4-nonene self-metathesis catalyzed by **2** with Me₄BTDP (X equiv), 0.1 mol% Mo, at 70 °C. X = 0.2 (blue diamonds), 0.5 (orange squares), 1 (green triangles), 2 (purple circles), and 5 (red crosses).

Figure 4. Synthesis and characterization of **2-(Me₄BTDP)_x**. (A) Reduction of **2** with Me₄BTDP. (B) XANES spectra of **2**, **2-(Me₄BTDP)₁**, and **2-(Me₄BTDP)₂**.

We evaluated the self-metathesis activity of this site-isolated molybdenum material with the *cis*-4-nonene (1000 equiv. to Mo), used as a prototypical substrate. Material **2** does not exhibit metathesis activity at 70 °C within 10 hours.^{§§} In the presence of 1 or 0.5 equiv. of Me₄BTDP at 70 °C, on the other hand, the equilibrium conversion is reached in ca. 90 minutes (Figure 3). Increasing or decreasing the amount of Me₄BTDP to 2 or 0.2 equiv. results in a lower activity. Note that at 30 °C the reaction also proceeds in the presence of 1 equiv. of Me₄BTDP, but it is slower: equilibration at 30 °C takes 24 h in comparison to 90 minutes at 70 °C (Figure S16). With ethyl oleate (100 equiv.), the conversion reaches only 30% after 24 h at 70 °C, showing that the reduced species are sensitive to functional groups or to possible impurities

present in the ethyl oleate substrate (Figure S21). Note also that the pre-reduced Mo supported materials prepared by treating **2** with 1 or 2 equiv. of Me₄BTDP (Figure 4A) – **2-(Me₄BTDP)_x** (X = 1, 2) – exhibit a slightly lower catalytic activity in the self-metathesis of *cis*-4-nonene compared to the in-situ reduced system (Figure S18 and Figure 3). This finding is similar to what was previously observed for W.²⁵ The IR spectra of **2-(Me₄BTDP)_x** reveal new C—H stretches at 2961 and 2903 cm⁻¹, indicating the presence of SiMe₃ groups that can be attributed to OSiMe₃ functionalities bound to Mo or the silica surface (Figure S3). A large decrease of the intensity of isolated silanol stretch at 3746 cm⁻¹ is also observed, which probably arises from the competitive reaction of Me₄BTDP with the surface silanols, leading to the passivation of the silica surface with SiMe₃ groups.²⁵ In addition, the signals at 1448 and 1415 cm⁻¹ suggest the binding of tetramethylpyrazine.

The reduction of the molybdenum centers in **2-(Me₄BTDP)_x** is confirmed by Mo K-edge XANES measurements (Figure 4B).³⁶ The edge energy for **2-(Me₄BTDP)₂** (20013.2 eV) is lower than for **2-(Me₄BTDP)₁** (20014.5 eV), suggesting that **2-(Me₄BTDP)₂** is more reduced than **2-(Me₄BTDP)₁**. The pre-edge peaks of both reduced materials are much smaller compared to **2**, indicating changes in geometries of the Mo centers after reduction. Besides, EPR measurements of **2-(Me₄BTDP)_x** showed absorption at around g=1.94, suggesting the presence of Mo(V) sites (Figure S10).^{36, 37} UV-vis-DRS measurements of those reduced species showed absorption in the 400-800 nm region, usually typical for d-d transition of reduced Mo species (Figure S9).³⁸

Reaction of the reduced species with carbon-13 labeled ethylene (see experimental details) shows the presence of 0.08 equiv. of propylene according to GC-MS. Propylene likely arises from the initial formation of a metallacyclopentane via oxidative coupling of two ethylene molecules followed by ring contraction (Figure 5),³⁹ suggesting the presence of ca. 8% of the active sites for the metathesis reaction, which is close to what is observed by reduction at high temperatures on related supported MoO_x species.⁴⁰ However, solid-state NMR of the materials does not show any signal associated with organometallic species (alkylidenes, metallacyclobutanes, or metallacyclopentanes), but poly(ethylene) instead (Figures

S4 and S5). The formation of poly(ethylene) is consistent with earlier work that shows that reduced Mo species can serve as polymerization catalysts.^{41, 42} This probably explains the low amounts of active sites observed above and illustrates the complexity of these supported catalysts once reduced.

Figure 5. The proposed mechanism for generating an alkylidene site.

In conclusion, we have developed a method to selectively generate well-defined $(\equiv\text{SiO})_2\text{Mo}(\text{O})_2$ on silica surface by grafting $\text{Mo}(\text{O})_2[\text{OSi}(\text{OtBu})_3]_2$ on SiO_{2-700} , followed by thermal treatment and calcination steps. Upon activation with Me_4BTDP the material catalyzes the self-metathesis of *cis*-4-nonene even at 30 °C. The XANES, UV-vis-DRS, and EPR analysis of $2\text{-(Me}_4\text{BTDP)}_x$ indicate the reduction of the molybdenum centers, which is probably an important step to generate the active species, an alkylidene or a metallacyclobutane, which have not been so far observed by NMR. Further work is currently under way to trap these intermediates.

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References

§ In the absence of a calcination step, reduced Mo species are formed as evidenced a slight change of color of the sample.

§§ In few instances, conversion was observed upon prolonging the reactions for several days.

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