Supporting information for:

Olefin-surface interactions: a key activity parameter in silica-supported olefin metathesis catalysts

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Experimental section

General procedures

All experiments were carried out under dry and oxygen-free nitrogen or argon atmosphere using Schlenk techniques or an MBraun or GS glovebox equipped with a purifier unit. Syntheses were carried out using high vacuum lines (10^{-5} mbar) and glovebox techniques. Toluene was purified using a double MBraun SPS alumina column. C_6H_6 and C_6D_6 were distilled from Na/benzophenone. 1,2-Dichlorobenzene and 1,1,2,2-tetrachloroethane were distilled from calcium hydride. Al_2O_3 was dried at 250 °C under high vacuum overnight. Molecular sieves were activated at 300 °C under high vacuum overnight. BASF Selexsorb® CD1/8” was calcined at 550 °C in air for 12 h and heated under high vacuum at 500°C for 2 h. All solvents were degassed by three consecutive freeze-pump-thaw cycles and stored over molecular sieves. The organosilicon reductant 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD) was prepared following literature procedures.[1] Elemental analyses were performed at Mikroanalytisches Labor Pascher, Germany. Solution 1H NMR spectra were recorded in C_6D_6 at room temperature using Bruker DRX 250 or DRX 300 NMR spectrometers and were referenced to the 1H signal from residual C_6H_6 at 7.16 ppm. All infrared (IR) spectra were recorded using a Bruker α-T spectrometer in an Ar glovebox equipped with OPUS software. A typical IR measurement consisted of acquisition of 32 scans in the region from 4000 to 400 cm^{-1}.

Catalyst syntheses

(≡SiO)2Mo(=O)2-red was prepared based on a previously reported procedure.[2] In brief, MoO_2[OSi(OtBu)_3]_2·(thf) was prepared following literature procedures.[3] Amorphous fumed silica (Aerosil Degussa, 200 m^2/g) was compacted with distilled water, calcined at 500 °C under
air for at least 4 h and treated under vacuum (10^{-5} \text{ mbar}) at 500 \degree C for 12 h and then at 700 \degree C for at least 12 h (ramp rate 1 \degree C/min), yielding dehydroxylated silica, denoted SiO_{2-700}. In a typical synthesis, a solution of 175.3 mg of MoO_{2}[OSi(OtBu)_{3}]_{2} \cdot \text{(thf)} in benzene/1,2-dimethoxyethane (1 M dme) was slowly added to a suspension of SiO_{2-700} (0.854 g, 1.06 equiv. Si-OH) in benzene at room temperature. The suspension was slowly stirred at room temperature for 16 h. The white solid was washed 5 times with benzene (2 mL) and the resulting solid was dried thoroughly under high vacuum (10^{-5} \text{ mbar}), yielding \((\equiv\text{SiO})_{2}\text{Mo}(\equiv\text{O})_{2}[\text{OSi(OtBu)}_{3}]\) as white particles. Analysis of the supernatant and the washing solution by \textsuperscript{1}H solution state NMR spectroscopy using ferrocene as an internal standard indicated the consumption of 0.52 equiv of MoO_{2}[OSi(OtBu)_{3}]_{2} \cdot \text{(thf)}. Elemental analysis of the grafted compound yielded 1.47 wt\% Mo. \((\equiv\text{SiO})_{2}\text{Mo}(\equiv\text{O})_{2}[\text{OSi(OtBu)}_{3}]\) was then loaded into a quartz flow reactor, placed under high vacuum (10^{-5} \text{ mbar}) and heated at 200 \degree C for 4 h followed by 400 \degree C (1\degree C/min) for 4 h. The reactor was cooled to ambient temperature under vacuum, after which it was placed under flow of synthetic air (passed through a purifier containing activated molecular sieves) and calcined at 400 \degree C (1\degree C/min) for 4 h, yielding \((\equiv\text{SiO})_{2}\text{Mo}(\equiv\text{O})_{2}\) as white particles. The material was then evacuated under high vacuum (10^{-5} \text{ mbar}) and stored in a glovebox under inert argon or nitrogen atmosphere prior to the catalytic reaction tests. Elemental analyses of separate batches of \((\equiv\text{SiO})_{2}\text{Mo}(\equiv\text{O})_{2}\) yielded 1.52-1.56 wt\% Mo. IR spectra of SiO_{2-700}, \((\equiv\text{SiO})_{2}\text{Mo}(\equiv\text{O})_{2}[\text{OSi(OtBu)}_{3}]\), and \((\equiv\text{SiO})_{2}\text{Mo}(\equiv\text{O})_{2}\) are shown in Figure S1. Immediately before catalytic reaction tests, \((\equiv\text{SiO})_{2}\text{Mo}(\equiv\text{O})_{2}\text{-red}\) was prepared by reduction of \((\equiv\text{SiO})_{2}\text{Mo}(\equiv\text{O})_{2}\) with 2 equiv. MBTCD per Mo in a benzene solution (0.08 mg/\mu L).

\textbf{MoO}_{2}\text{@SiO}_{2}\text{-red}\ was prepared following an incipient wetness impregnation approach based on literature procedures\textsuperscript{[4]}: Amorphous fumed silica (Aerosil Degussa, 200 m\textsuperscript{2}/g) with a pore volume of ca. 1.5 cm\textsuperscript{3}/g found by N\textsubscript{2} adsorption was calcined under flowing synthetic air (30 standard
cubic centimeters per minute, sccm) at 500 °C to remove adsorbed organics. Freshly calcined SiO$_2$ (1 g) in a glass flask was impregnated with 1.5 mL/g of an aqueous solution of (NH$_4$)$_6$Mo$_7$O$_{24}$·(H$_2$O)$_4$ in milliQ water (55 mg/mL). The (NH$_4$)$_6$Mo$_7$O$_{24}$·(H$_2$O)$_4$ solution was added in 100 μL increments while stirring with a glass stir rod. The impregnated silica was allowed to dry overnight under ambient conditions, then loaded into a glass flow reactor and heated under flowing synthetic air to 80 °C for 4 h, 110 °C for 4 h, and finally calcined at 500 °C for 4 h (ramp rate 1 °C/min.). The resultant material (MoO$_x$@SiO$_2$) was then evacuated under high vacuum (10$^{-5}$ mbar) and stored in a glovebox under inert argon or nitrogen atmosphere prior to the catalytic reaction tests. Elemental analysis of MoO$_x$@SiO$_2$ yielded 3.52 wt% Mo. The IR spectrum of MoO$_x$@SiO$_2$ is shown in Figure S2. Immediately before catalytic reaction tests, MoO$_x$@SiO$_2$-red was prepared by reduction of MoO$_x$@SiO$_2$ with 2 equiv. MBTCD per Mo in a benzene solution (0.08 mg/μL).

The cationic Mo alkylidenes Mo$^+$ and Mo$^+$/SiO$_2$-700 were synthesized as previously reported.$^{[5,6]}$

**Substrate preparation**

1-Octene (>95%), 1-nonene (>95%), 1-tridecene (>95%), 1-hexadecene (>95%), and 1-eicosene (>95%) were obtained from Tokyo Chemical Industry (TCI). Decalin (98%) was obtained from Acros Organics for use as an internal standard. All substrates and decalin were rigorously purified$^{[7]}$ by drying overnight over sodium metal, distillation *in vacuo*, degassing by at least three freeze-pump-thaw cycles, and storage in the glovebox. Before the preparation of the olefin stock solutions, the neat olefins were stored over BASF Selexsorb® for 4 h and filtered 3x through a pad of activated alumina. After this purification protocol the substrates were found to be typically ca. 97% pure by GC, with the impurities being predominantly internal isomers of the terminal olefins.
Note that prolonged exposure to Selexsorb or molecular sieves promotes isomerization of the terminal olefins to their internal isomers.\textsuperscript{[7]} Decalin was passed 3 times through a pad of activated alumina and stored over Selexsorb. 1 M stock solutions of the terminal olefins in 1,2-dichlorobenzene with 0.1 M decalin as an internal standard were prepared before the catalytic tests and used immediately.

\textbf{Catalytic activity measurements}

The terminal olefin metathesis reactions were conducted in a nitrogen-filled glovebox using the High-Throughput Experimentation facility at ETH Zürich (HTE@ETH). The catalysts were weighed out into 10 mL reaction vials, heated to the reaction temperature (30 or 70 °C), and shaken at 300 rpm. The reaction vials were either left open over the course of the reaction to allow for ethylene removal or closed with a Teflon plate. 30 μL aliquots of the reaction mixture were taken at the specified time points, diluted with 600 μL toluene, and analyzed by GC/FID. Conversions were calculated from substrate concentration, while product formation rates were calculated from the concentrations of the metathesis products.

\textit{Preparation of post-reaction catalysts for spectroscopic analysis}

After reaction of (≡SiO)\textsubscript{2}Mo(=O)\textsubscript{2}-red of Mo\textsuperscript{7}/SiO\textsubscript{2-700} with 1-hexadecene or 1-nonene for the specified reaction time at 30 °C, the reaction solution was filtered off and the post-reaction catalyst was washed with benzene (3x 1 mL), dried overnight under high vacuum (<10\textsuperscript{-5} mbar), and transferred into a glovebox where the dried material was powdered and packed into an NMR rotor.

\textit{Preparation of olefin-adsorbed SiO\textsubscript{2-700}}

The adsorption of olefins on silica devoid of Mo centers was also tested by contacting dehydroxylated silica SiO\textsubscript{2-700} with olefin solution for 3 h, after which the material was filtered
from the olefin solution, washed with benzene (3x 1 mL), and dried overnight under high vacuum (<10⁻⁵ mbar). The olefin solution was either 1 M 1-hexadecene or 0.35 M 15-triacontene, the product of 1-hexadecene metathesis which was purified by vacuum distillation (est. >95% purity by GC).

**Solid-state NMR analyses**

The 1D and 2D solid-state \(^1\)H and \(^1\)H{\(^{13}\)C} NMR spectra were acquired on a 700 MHz (16.4 T) Bruker NMR spectrometer equipped with a 1.3 mm HX MAS probe head and operating at Larmor frequencies of 176.061 and 700.135 MHz for \(^{13}\)C and \(^1\)H, respectively. The rotors were transferred to the NMR spectrometer in a tightly sealed vial with a screw-cap top, rapidly inserted into the MAS probe head, and spun with dry N₂ gas. MAS rates of 50 kHz were used with relaxation delays of 3.5 s, which was ca. 1.4 times the longest measured \(^1\)H spin-lattice \(T_1\) relaxation time (measured by \(^1\)H saturation recovery). The measurements used \(^1\)H \(\pi/2\) pulse lengths of 2 μs (125 kHz) and \(^{13}\)C \(\pi/2\) pulse lengths of 3 μs (83 kHz). The 2D \(^1\)H{\(^{13}\)C} correlation spectrum was acquired using a 2D dipolar-mediated HMQC sequence with 60 rotor periods of SR₄ recoupling to reintroduce the \(^1\)H-\(^{13}\)C dipole-dipole couplings. 64 \(t_1\) increments were used in the indirect dimension and 480 transients for a total acquisition time of 30 h. \(^1\)H spin-spin \(T_2\) relaxation times were measured using a pseudo-2D CPMG sequence with varied lengths (\(\tau\)) of rotor-synchronized echo trains.

The 1D and 2D \(^{13}\)C{\(^1\)H} and \(^{29}\)Si{\(^1\)H} DNP-NMR spectra were acquired on a Bruker Avance III 600 MHz (14.1 T) DNP NMR spectrometer equipped with low-temperature 3.2 mm triple-resonance MAS cryo-probe operating at Larmor frequencies of 599.900, 150.858, 119.166 MHz for \(^1\)H, \(^{13}\)C, and \(^{29}\)Si, respectively. For the DNP-enhanced NMR measurements, (≡SiO)₂Mo(≡O)₂-red was reacted with 1-hexadecene for 4 h, washed and dried as described above, and transferred
into a glovebox where the dried material was ground and impregnated with a 16 mM solution of TEKPol biradical\[^{[10]}\] in 1,1,2,2-tetrachloroethane. The material was then packed into a sapphire MAS NMR rotor with a zirconia cap, transferred to the NMR spectrometer in a tightly sealed vial with a screw-cap top and rapidly inserted into pre-cooled (100 K) MAS NMR probe head. DNP-NMR measurements were acquired at 10 kHz MAS under continuous microwave irradiation at 395 GHz. The microwave on/off DNP enhancements were measured by comparison of the \(^{13}\text{C}\{^{1}\text{H}\}\) CPMAS spectra acquired with and without microwave irradiation and were found to be ca. 4 for the \(^{13}\text{C}\) signals associated with surface-bound organic species. For all DNP-NMR measurements, a relaxation delay of 3 s was used. The 2D \(^{29}\text{Si}\{^{1}\text{H}\}\) DNP-HETCOR spectra in Figures 5 and S20 were acquired with \(^{29}\text{Si}-^{1}\text{H}\) contact times of 0.5 or 5 ms, 512 transients, and 16 or 30 \(t_1\) increments in the indirect dimension for total acquisition times of 7 or 13 h, respectively. The 2D \(^{13}\text{C}\{^{1}\text{H}\}\) DNP-HETCOR spectrum in Figure S19 was acquired with a \(^{13}\text{C}-^{1}\text{H}\) contact times of 2 ms, 64 transients, and 64 \(t_1\) increments in the indirect dimension for total acquisition time of 3.5 h. All of the 2D DNP-NMR spectra were acquired with 100 kHz eDUMBO homonuclear decoupling\[^{[11]}\] in the indirect \(^{1}\text{H}\) dimension and 100 kHz SPINAL-64 heteronuclear \(^{1}\text{H}\) decoupling\[^{[12]}\] during the acquisition period.

\textit{Ab initio Molecular dynamics simulations}

Olefin geometries were pre-optimized using the hybrid functional B3LYP\[^{[13–17]}\] in combination with the 6-31g(d) basis set\[^{[18]}\] in Gaussian 09 (revision d1).\[^{[19]}\] Before ab initio molecular dynamics (AIMD) run the structure were optimized using the conjugated gradient method (convergence criteria) in the CP2K (3.0) program.\[^{[20]}\] The revPBE\[^{[21–23]}\] functional including Grimme dispersion correction\[^{[24]}\] and Becke-Johnson damping functions (D3-BJ)\[^{[24,25]}\] was used in combination with the double-zeta (DZVP-MOLOPT-SR-GTH)\[^{[26]}\] basis set and the associated GTH
pseudopotential.\cite{27} For the AIMD calculation, the olefin was placed on previously optimized silica surface model (cell size 21.4 Å x 21.4 Å x 34.2 Å)\cite{28} and the system was optimized using the same level of theory.

The system was then equilibrated at 295 K in the NVT ensemble using a 1 fs for each of the 3000 steps and the temperature was controlled using a 295 K canonical sampling through velocity rescaling (CSVR) thermostat \cite{29} (time step 100 fs). All hydrogen atoms were substituted by deuterium ones in order to allow a longer time step and it prevents artificial bond breaking due to the fast motion of H atoms. Further a weak external potential of the form $1 \times 10^{-12} \times (Z-12)^4$ was added to disfavor desorption of the olefin from the surface. The four lowest energy structures for each olefin found by AIMD were again optimized with the same level of theory in CP2K to obtain optimized geometries of the olefins at the surface. From these four geometries the values in Table S7 were extracted.
FTIR Spectra of as-prepared (pre)catalysts

![FTIR Spectra](image)

Figure S1. Transmission FTIR spectra of (a) SiO$_2$-700, (b) grafted molecular Mo dioxo siloxide (≡SiO)$_2$Mo(=O)$_2[OSi(OtBu)$_3$], and (c) (≡SiO)$_2$Mo(O)$_2$.

![FTIR Spectrum](image)

Figure S2. Transmission FTIR spectrum of MoO$_x$/SiO$_2$.
Figure S3. Transmission FTIR spectra of (a) SiO$_2$-700 and (b) Mo$/$/SiO$_2$. 
Catalytic reaction data

Figure S4. Metathesis of 1-nonene by (≡SiO)2Mo(=O)2-red at 70 °C. Open reaction vial, ca. 0.1 mol% Mo.

Figure S5. Metathesis of 1-nonene by (≡SiO)2Mo(=O)2-red at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.
Figure S6. Metathesis of 1-nonene by \((=\text{SiO})_2\text{W}(=\text{O})_2\) at 70 °C. Open reaction vial, ca. 0.1 mol% W.

Figure S7. Metathesis of 1-nonene by \(\text{MoO}_x/\text{SiO}_2\) at 70 °C. Open reaction vial, ca. 0.1 mol% Mo.
Figure S8. Metathesis of 1-nonene by MoO$_3$/SiO$_2$-red at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.
Table S1. Summary of catalytic data for metathesis of 1-nonene by $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$-red, $(\equiv\text{SiO})_2\text{W}(=\text{O})_2$-red, and MoO$_x$/SiO$_2$-red.<sup>a</sup>

| Catalyst                  | Temperature (°C) | Maximum product formation rate (mmol product/[mmol Mo min])<sup>b</sup> | Initial product E/Z ratio<sup>b</sup> | Substrate conversion after 4 h (%) | Selectivity for olefin metathesis product (%) |
|---------------------------|------------------|---------------------------------------------------------------------|--------------------------------------|----------------------------------|--------------------------------------------|
| $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$-red | 70               | 2.6                                                                 | 2.11                                 | 45                               | 89                                         |
| $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$-red | 30               | 2.6                                                                 | 2.34                                 | 54                               | 99                                         |
| $(\equiv\text{SiO})_2\text{W}(=\text{O})_2$-red | 70               | 0.7                                                                 | 1.45                                 | 20                               | 99                                         |
| MoO$_x$/SiO$_2$-red       | 70               | 3.9                                                                 | 2.07                                 | 66                               | 94                                         |
| MoO$_x$/SiO$_2$-red       | 30               | 0.9                                                                 | 2.35                                 | 32                               | 98                                         |

<sup>a</sup> Conditions: 70 or 30 °C, open reaction vials, 2.5 mL reaction volume, substrate : Mo = 1000 : 1 (ca. 0.1 mol% Mo)

<sup>b</sup> Measured between 10 and 13 minutes reaction time for each catalyst.
Figure S9. 1-nonene metathesis product E (red) and Z (blue) selectivity for (a) \((\equiv\text{SiO})_2\text{Mo(=O)}_2\)-red and (b) MoO\(_x\)/SiO\(_2\)-red at 70 °C.

Figure S10. 1-nonene metathesis product E (red) and Z (blue) selectivity for (a) \((\equiv\text{SiO})_2\text{Mo(=O)}_2\)-red and (b) MoO\(_x\)/SiO\(_2\)-red at 30 °C.
Figure S11. Metathesis of 1-octene by ($\equiv$SiO)$_2$Mo($\equiv$O)$_2$-red at 70 °C. Closed reaction vial, ca. 0.1 mol% Mo.

Figure S12. Metathesis of 1-nonene by ($\equiv$SiO)$_2$Mo($\equiv$O)$_2$-red at 70 °C. Closed reaction vial, ca. 0.1 mol% Mo.
Figure S13. Metathesis of 1-tridecene by (mSiO)$_2$Mo(=O)$_2$-red at 70 °C. Closed reaction vial, ca. 0.1 mol% Mo.

Figure S14. Metathesis of 1-hexadecene by (mSiO)$_2$Mo(=O)$_2$-red at 70 °C. Closed reaction vial, ca. 0.1 mol% Mo.
Figure S15. Metathesis of 1-eicosene by (Si=O)2Mo(=O)2-red at 70 °C. Closed reaction vial, ca. 0.2 mol% Mo.

Table S2. Summary of catalytic data for metathesis of linear α-olefins by (Si=O)2Mo(=O)2-red at 70 °C. a

| Substrate   | Maximum product formation rate (mmol product/[mmol Mo min])b | Initial product E/Z ratiob | Substrate conversion after 4 h (%) | Selectivity for olefin metathesis product (%) |
|-------------|-------------------------------------------------------------|-----------------------------|-----------------------------------|---------------------------------------------|
| 1-octene    | 9.9                                                         | 2.36                        | 78                                | 85                                          |
| 1-nonene    | 8.1                                                         | 2.41                        | 43                                | 97                                          |
| 1-tridecane | 4.5                                                         | 2.33                        | 67                                | 96                                          |
| 1-hexadecane| 2.7                                                         | 2.30                        | 69                                | 91                                          |
| 1-eicosene  | 0.9                                                         | -c                          | 25                                | -c                                          |

a Conditions: 70 °C, closed reaction vials, 2.5 mL reaction volume, substrate : Mo = 1000 : 1 (ca. 0.1 mol% Mo) for 1-octene, 1-nonene, 1-tridecane, and 1-hexadecene, substrate : Mo = 500 : 1 (ca. 0.2 mol% Mo) for 1-eicosene
b Measured between 10 and 13 minutes reaction time for each catalyst
c Product peaks not resolved
Figure S16. Metathesis of 1-octene by \((\equiv\text{SiO})_2\text{Mo}(=\text{O})_2\)-red at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.

Figure S17. Metathesis of 1-nonene by \((\equiv\text{SiO})_2\text{Mo}(=\text{O})_2\)-red at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.
Figure S18. Metathesis of 1-tridecene by \((\equiv \text{SiO})_2\text{Mo}(=\text{O})_2\text{-red}\) at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.

Figure S19. Metathesis of 1-hexadecene activity of \((\equiv \text{SiO})_2\text{Mo}(=\text{O})_2\text{-red}\) at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.
Figure S20. Metathesis of 1-eicosene by (≡SiO)₂Mo(=O)₂-red at 30 °C. Open reaction vial, ca. 0.2 mol% Mo.

Table S3. Summary of catalytic data for metathesis of linear α-olefins by (≡SiO)₂Mo(=O)₂-red at 30 °C.ᵃ

| Substrate     | Maximum product formation rate (mmol product/[mmol Mo min])ᵇ | Initial product E/Z ratioᵇ | Substrate conversion after 4 h (%) | Selectivity for olefin metathesis product (%) |
|---------------|---------------------------------------------------------------|-----------------------------|-----------------------------------|-----------------------------------------------|
| 1-octene      | 3.2                                                           | 2.50                        | 60                               | 98                                            |
| 1-nonene      | 2.6                                                           | 2.34                        | 54                               | 99                                            |
| 1-tridecane   | 2.0                                                           | 2.33                        | 55                               | 99                                            |
| 1-hexadecane  | 1.6                                                           | 2.43                        | 39                               | 97                                            |
| 1-eicosene    | 0.6                                                           | -ᶜ                         | 9                                | -ᶜ                                            |

ᵃConditions: 30 °C, open reaction vials, 2.5 mL reaction volume, substrate : Mo = 1000 : 1 (ca. 0.1 mol% Mo) for 1-octene, 1-nonene, 1-tridecane, and 1-hexadecene, substrate : Mo = 500 : 1 (ca. 0.2 mol% Mo) for 1-eicosene
ᵇMeasured between 10 and 13 minutes reaction time for each catalyst
ᶜProduct peaks not resolved
Figure S21. Metathesis of 1-nonene by MoO₃/SiO₂-red at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.

Figure S22. Metathesis of 1-tridecene by MoO₃/SiO₂-red at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.
Figure S23. Metathesis of 1-hexadecene by MoO$_x$/SiO$_2$-red at 30 °C. Open reaction vial, ca. 0.1 mol% Mo.

Table S4. Summary of catalytic data for metathesis of linear $\alpha$-olefins by MoO$_x$/SiO$_2$-red at 30 °C.$^a$

| Substrate       | Maximum product formation rate (mmol product/[mmol Mo min]) at the indicated reaction time | Initial product E/Z ratio$^b$ | Substrate conversion after 4 h (%) | Selectivity for olefin metathesis product (%) |
|-----------------|-------------------------------------------------------------------------------------------------|-------------------------------|-----------------------------------|-----------------------------------------------|
| 1-nonene        | 0.9 (14 minutes)                                                                                | 2.35                          | 32                               | 98                                            |
| 1-tridecane     | 0.7 (60 minutes)                                                                                | 2.29                          | 33                               | 98                                            |
| 1-hexadecane    | 0.5 (60 minutes)                                                                                | 2.30                          | 25                               | 99                                            |

$^a$ Conditions: 30 °C, open reaction vials, 2.5 mL reaction volume, substrate : Mo = 1000 : 1 (ca. 0.1 mol% Mo)

$^b$ Measured after 10-14 minutes of reaction time
Figure S24. Metathesis of 1-octene by Mo⁺ at 30 °C. Open reaction vial, ca. 0.02 mol% Mo.

Figure S25. Metathesis of 1-nonene by Mo⁺ at 30 °C. Open reaction vial, ca. 0.02 mol% Mo.
Figure S26. Metathesis of 1-tridecene by Mo⁺ at 30 °C. Open reaction vial, ca. 0.02 mol% Mo.

Figure S27. Metathesis of 1-hexadecene by Mo⁺ at 30 °C. Open reaction vial, ca. 0.02 mol% Mo.
Figure S28. Metathesis of 1-eicosene by Mo+ at 30 °C. Open reaction vial, ca. 0.04 mol% Mo.
Table S5. Summary of catalytic data for metathesis of linear α-olefins by Mo⁺ at 30 °C.⁹

| Substrate     | Maximum product formation rate (mmol product/[mmol Mo min])³ | Initial product E/Z ratio⁴ | Substrate conversion after 1 h (%) | Selectivity for olefin metathesis product (%) |
|---------------|--------------------------------------------------------------|-----------------------------|-----------------------------------|-----------------------------------------------|
| 1-octene      | 250                                                          | 4.31                        | 91                                | 99                                           |
| 1-nonene      | 350                                                          | 4.05                        | 96                                | 96                                           |
| 1-tridecane   | 322                                                          | 3.8                         | 86                                | 97                                           |
| 1-hexadecane  | 310                                                          | 3.81                        | 92                                | 97                                           |
| 1-eicosene    | 365                                                          | -c                         | 78                                | -c                                           |

⁹Conditions: 30 °C, open reaction vials, 2.5 mL reaction volume, substrate : Mo = 5000 : 1 (ca. 0.02 mol% Mo) for 1-octene, 1-nonene, 1-tridecane, and 1-hexadecane, 2500 substrate : 1 Mo (ca. 0.04 mol% Mo) for 1-eicosene

³Measured between 3 and 4.5 minutes reaction time for each catalyst

⁴Product peaks not resolved
**Figure S29.** Metathesis of 1-octene by Mo+/SiO2 at 30 °C. Open reaction vial, ca. 0.02 mol% Mo.

**Figure S30.** Metathesis of 1-nonene by Mo+/SiO2 at 30 °C. Open reaction vial, ca. 0.02 mol% Mo.
Figure S31. Metathesis of 1-tridecene by Mo+/SiO2 at 30 °C. Open reaction vial, ca. 0.02 mol% Mo.

Figure S32. Metathesis of 1-hexadecene by Mo+/SiO2 at 30 °C. Open reaction vial, ca. 0.02 mol% Mo.
| Substrate    | Maximum product formation rate (mmol product/[mmol Mo min])<sup>b</sup> | Initial product E/Z ratio<sup>b</sup> | Substrate conversion (%) after reaction time in parentheses (minutes) | Selectivity for olefin metathesis product (%) |
|--------------|---------------------------------------------------------------------|-------------------------------------|---------------------------------------------------------------------|---------------------------------------------|
| 1-octene     | 300                                                                 | 4.6                                 | 98 (60)                                                             | 95                                          |
| 1-nonene     | 460                                                                 | 3.2                                 | 95 (60)                                                             | 96                                          |
| 1-tridecene  | 380                                                                 | 3.8                                 | 90 (30)                                                             | 97                                          |
| 1-hexadecene | 250                                                                 | 3.8                                 | 93 (60)                                                             | 97                                          |
| 1-eicosene   | 365                                                                 | c                                   | 40 (3)                                                              | c                                           |

<sup>a</sup>Conditions: 30 °C, open reaction vials, 2.5 mL reaction volume, substrate : Mo = 5000 : 1 (ca. 0.02 mol% Mo) for 1-octene, 1-nonene, 1-tridecene, and 1-hexadecene, 2500 substrate : 1 Mo (ca. 0.04 mol% Mo) for 1-eicosene

<sup>b</sup>Measured between 3 and 4.5 minutes reaction time for each catalyst

<sup>c</sup>Product peaks not resolved
Figure S33. Comparison of two separate 1-nonene metathesis reaction tests by (a) Mo\(^+\) (b) Mo\(^+\)/SiO\(_2\). Open reaction vials, ca. 0.02 mol% Mo. TOF\(_{3\text{min}}\) values from the two tests are 350 and 330 for Mo\(^+\) and 400 and 450 for Mo\(^+\)/SiO\(_2\). Combined with experimental uncertainties, this yields an estimated error of +/- 40 on the TOF values for these highly active catalysts.

Figure S34. Comparison of reactivity trends for Mo\(^+\) at 30 °C (blue), Mo\(^+\)/SiO\(_2\) at 30 °C (orange), (Si=O)\(_2\)Mo(=O)\(_2\)-red at 30 °C (green), and (Si=O)\(_2\)Mo(=O)\(_2\)-red at 70 °C (red) as a function of substrate carbon number. For each catalyst, the initial reaction rate was normalized by that of 1-nonene.
Spectroscopic and elemental analyses of post-reaction catalysts

Table S7. Elemental analyses of \((=\text{SiO})_2\text{Mo}(=\text{O})_2\text{-red}\) before and after 1-hexadecene metathesis at 30 °C\(^a\)

| Material                      | Reaction time (h) (%) conv. | Carbon content (wt%) | Molecules per nm\(^2\) | Minimum fractional surface coverage\(^b\) | Maximum fractional surface coverage\(^c\) |
|-------------------------------|-----------------------------|----------------------|-------------------------|------------------------------------------|------------------------------------------|
| \(\text{SiO}_2\text{-700 contacted with 15-triacontene}\) | -                           | 3.3                  | 0.28                    | 0.2                                      | 0.5                                      |
| \((=\text{SiO})_2\text{Mo}(=\text{O})_2\text{-red}\)     | 0 (0)                       | 0.9\(^d\)            | -                       | -                                        | -                                        |
| \((=\text{SiO})_2\text{Mo}(=\text{O})_2\text{-red}\)     | 1 (8)                       | 1.8                  | 0.15                    | 0.1                                      | 0.3                                      |
| \((=\text{SiO})_2\text{Mo}(=\text{O})_2\text{-red}\)     | 3 (35)                      | 5.0                  | 0.42                    | 0.3                                      | 0.7                                      |

\(^a\) Conditions: 30 °C, open reaction vials, 3 mL reaction volume, substrate : Mo = 1000 : 1

\(^b\) Estimated assuming the sole organic on the surface is 15-triacontene, with a minimal projected area of 0.75 nm\(^2\) and a surface area of 200 m\(^2\)/g

\(^c\) Estimated assuming the sole organic on the surface is 15-triacontene, with a maximal projected area of 1.7 nm\(^2\) and a surface area of 200 m\(^2\)/g

\(^d\) Arising from residual -TMS groups of the organosilicon reductant.
Figure S35. Transmission FTIR spectra of \((=\text{SiO})_2\text{Mo(O)}_2\text{-red}\) (a) before and after 1-hexadecene metathesis at 30 °C for (b) 1 hour (ca. 8% conversion) or (c) 3 hours (ca. 35% conversion). Each material was washed 3x with benzene and dried overnight at \(10^{-5}\) mbar. (d) Expansion and overlay of the \(-\text{OH}\) stretch region for the three spectra in (a-c), showing the decrease in intensity of the signal from isolated SiOH at 3745 cm\(^{-1}\) with concomitant emergence of broad signals at 3695 and 3606 cm\(^{-1}\), consistent with interactions of isolated SiOH species with adsorbed olefin metathesis products.
Figure S36. Solid-state 1D $^1$H echo MAS NMR spectrum of ($\equiv$SiO)$_2$Mo(O)$_2$-red after 1-hexadecene metathesis at 30 °C for (a) 1 hour (ca. 8% conversion), (b) 3 hours (ca. 35% conversion), or (c) 24 hours (ca. 80% conversion), followed by washing 3x with benzene and drying overnight at $10^{-5}$ mbar. The spectra were acquired at 40 kHz MAS, 16.4 T, and 298 K.
Figure S37. Solid-state $^1$H MAS NMR echo spectra of (Si=O)$_2$Mo(=O)$_2$-red after 24 h reaction with 1-hexadecene (top) or 1-nonene (bottom) in 1,2-dichlorobenzene at 30 °C, 3x washing with C$_6$H$_6$, and drying under high vacuum. The spectra were acquired at 16.4 T, 50 kHz MAS, and 280 K. After reaction with 1-nonene, a much more prominent signal is observed at 7.3 ppm from aromatic moieties of solvent molecules compared to after reaction with 1-hexadecene. This suggests that physisorption of solvent molecules is competitive with that of the olefin metathesis product molecules.
Figure S38. Solid-state 2D $^{13}$C{¹H} DNP-HETCOR spectra of ($≡$SiO)$_2$Mo($≡$O)$_2$ after 4 h reaction with 1-hexadecene in 1,2-dichlorobenzene at 30 °C, 3x washing with C$_6$H$_6$, and drying under high vacuum. The 2D spectrum was acquired at 14.1 T, 12.5 kHz MAS, 100 K, under continuous microwave irradiation at 395 GHz, in the presence of 16 mM TEKPol biradical in 1,1,2,2-tetrachloroethane (DNP solvent), and with a $^{13}$C-¹H contact time of 1 ms. A 1D $^{13}$C{¹H} DNP-CPMAS spectrum acquired under the same conditions is shown along the horizontal axis for comparison with the 1D $^{13}$C projection of the 2D spectrum.

Discussion of signal assignments for Figure S38

The $^1$H signal at 0.0 ppm is assigned to -TMS moieties based on its correlation in Fig. S36 to a $^{13}$C signal at 0 ppm (purple shaded region in Figure S36). The $^1$H signals at 0.7 to 2.7 ppm are assigned to aliphatic moieties (green shaded regions in Fig. 5 and S36) based on their correlation to $^{13}$C signals at 14, 23, and 31 ppm. The $^1$H signals from 5.8 to 6.4 ppm (grey shaded regions) are assigned to DNP solvent molecules (1,1,2,2-tetrachloroethane) based on their correlation in Fig. S36 to $^{13}$C signals at 78 ppm. The $^1$H signals from 4.4 to 5.6 ppm are correlated in Fig. S36 to the
$^{13}$C signal at 31 ppm from allylic $^{13}$C moieties and are assigned to olefinic moieties. There are no correlations of these signals to the $^{13}$C signals from olefinic moieties at 116 and 128 ppm observed in Fig. S36 likely because of their low signal intensity and spectral broadening under the low-temperature measurement conditions. Nevertheless, the signal assignments are corroborated by the correlation of the $^1$H signal at 5.6 ppm to the $^{13}$C signal at 132 ppm in the $^1$H$^{13}$C D-HMQC spectrum acquired at room temperature in Figure 4. Finally, the $^1$H signals between 7.1 to 8.5 ppm are assigned to aromatic species (e.g., 1,2-dichlorobenzene, blue shaded regions) based on the weak correlation of the $^1$H signal at 7.1 ppm to the $^{13}$C signal at 128 ppm in Figure S36. We note that $^1$H signals at $>7$ ppm could also arise in part from strongly hydrogen-bonded or hydrated -OH moieties, as have been previously observed under DNP-NMR conditions for silicate and aluminosilicate zeolites$^{49,50}$ and other silica based materials,$^{51}$ though such species are expected to be dilute in the dehydroxylated supported catalyst ($=\text{SiO}_2\text{Mo(=O)}_2$-red).
Figure S39. Solid-state 2D $^{29}$Si-$^1$H DNP-HETCOR spectrum of (mSiO)$_2$Mo(=O)$_2$-red after 4 h reaction with 1-hexadecene in 1,2-dichlorobenzene at 30 °C, 3x washing with C$_8$H$_6$, and drying under high vacuum. The 2D spectrum was acquired at 14.1 T, 12.5 kHz MAS, 100 K, under continuous microwave irradiation at 395 GHz, in the presence of 16 mM TEKPol biradical in 1,1,2,2-tetrachloroethane (DNP solvent), and with a $^{29}$Si-$^1$H contact time of 5 ms. (Same spectrum as Figure 5b in the main text with an expanded frequency axis showing the signals arising from surface -OTMS moieties).
Table S8. $^1$H $T_2$ relaxation analyses extracted from solid-state $^1$H CPMG spectra of ($\equiv$SiO)$_2$Mo(=O)$_2$-red after 24 h reaction with 1-hexadecene or 1-nonene in 1,2-dichlorobenzene at 30 °C, 3x washing with C$_6$H$_6$, and drying under high vacuum. The spectra were acquired at 16.4 T, 50 kHz MAS, 280 K, and with varying numbers of CPMG loops. The integrated signal intensities were extracted using the DMFIT software$^{[30]}$ and fit to stretched exponential fitting functions$^{[31]}$ to extract the characteristic $T_2$ relaxation rate of the corresponding $^1$H species and the stretched exponent, $\beta$.

| $^1$H signal position | Assignment         | $T_2$ (ms) | $\beta$ |
|-----------------------|--------------------|-----------|---------|
|                       | ($\equiv$SiO)$_2$Mo(=O)$_2$-red after 1-hexadecene metathesis |           |         |
| 0.3                   | -SiCH$_3$          | 7.2       | 0.35    |
| 1.0                   | -CH$_3$            | 2.6       | 0.88    |
| 1.5                   | Aliphatic -CH$_2$- | 2.3       | 0.90    |
| 2.2                   | Allylic -CH$_2$-   | 1.9       | 0.77    |
| 5.6                   | Olefinic -CH=      | 1.9       | 0.80    |
| 7.3                   | Physisorbed solvent| 0.1       | 0.27    |
|                       | ($\equiv$SiO)$_2$Mo(=O)$_2$-red after 1-nonene metathesis |           |         |
| 0.3                   | -SiCH$_3$          | 26.9      | 0.62    |
| 1.0                   | -CH$_3$            | 2.3       | 0.48    |
| 1.5                   | Aliphatic -CH$_2$- | 1.3       | 0.45    |
| 2.2                   | Allylic -CH$_2$-   | 1.5       | 0.36    |
| 7.3                   | Physisorbed solvent| 0.3       | 0.14    |
Figure S40. Transmission FTIR spectra of SiO$_2$-700 (a) as prepared or contacted for 3 hours with (b) 1 M 1-hexadecene or (c) 0.3 M 15-triacontene (distilled product of 1-hexadecene metathesis) in dichlorobenzene followed by washing 3x with benzene and drying overnight at 10$^{-5}$ mbar.
Figure S41. Solid-state 1D $^1$H echo MAS NMR spectrum of SiO$_2$-700 contacted for 3 hours with (a) 1 M 1-hexadecene or (b) 0.3 M 15-triacontene (distilled product of 1-hexadecene metathesis) in dichlorobenzene followed by washing 3x with benzene and drying overnight at 10$^{-5}$ mbar.
Figure S42. Transmission FTIR spectra of Mo\textsuperscript{+}/SiO\textsubscript{2} (a) before and (b) after 1-hexadecene metathesis at 30 °C for 1 hour, followed by washing 3x with benzene and drying overnight at 10\textsuperscript{-5} mbar. Signals at 2320 and 2295 cm\textsuperscript{-1} from acetonitrile are removed, indicating decoordination of acetonitrile under reaction conditions. Signals in the 1300-1600 cm\textsuperscript{-1} region are also reduced in intensity likely due to remove of the aromatic –C(Me)\textsubscript{2}Ph alkylidene moiety on catalyst initiation. Notably, the signals from SiOH species at 3700 and 3615 cm\textsuperscript{-1} are minimally perturbed after reaction, indicating that these OH sites participate little in olefin metathesis product adsorption.
## Summary of MD simulation results

**Table S9.** Summary of AIMD simulation results of olefin interactions with a model for amorphous silica.

| Compound     | Average adsorption energy a (kJ/mol) | Lowest adsorption energy a (kJ/mol) | Distances between vinylic H atoms of olefin and closest O atom of surface OH (Å)b | Distances between vinylic H atoms of olefin and O atoms of surface siloxane bridges (Å)b |
|--------------|-------------------------------------|-------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| 1-propene    | -114.91                             | -123.47                             | 2.70                                                                              | 2.84                                                                              |
| 1-hexene     | -144.85                             | -167.38                             | 3.37                                                                              | 3.44                                                                              |
| 1-octene     | -132.81                             | -138.81                             | 3.78                                                                              | 4.18                                                                              |
| 1-nonene     | -127.80                             | -139.44                             | 4.21                                                                              | 4.63                                                                              |
| 1-decene     | -157.57                             | -175.65                             | 2.35                                                                              | 2.46                                                                              |
| E-2-butene   | -129.40                             | -136.64                             | 2.38                                                                              | 2.44                                                                              |
| E-3-hexene   | -138.21                             | -147.68                             | 2.36                                                                              | 2.39                                                                              |
| E-4-octene   | -123.27                             | -140.15                             | 4.30                                                                              | 4.32                                                                              |
| E-5-decene   | -148.74                             | -157.99                             | 2.84                                                                              | 3.25                                                                              |
| Z-5-decene   | -153.60                             | -173.16                             | 2.74                                                                              | 2.91                                                                              |

*a* Of the four lowest energy structures found for each olefin

*b* From lowest energy structure found for each olefin

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