

SUPPORTING INFORMATION

METATHETIC OXIDATION OF 2-BUTENES TO ACETALDEHYDE BY MOLECULAR OXYGEN USING THE SINGLE-SITE OLEFIN METATHESIS CATALYST ($\equiv\text{SiO}_2\text{Mo}(\text{=O})_2$).

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Supporting Section 1 *Materials and General Procedures*

All experiments were carried out using standard air-free methodology in an argon-filled glovebox, on a Schlenk line or in a Schlenk-type apparatus interfaced to a high-vacuum line (10^{-5} mbar). Grafting is performed in double Schlenk flask that allows filtration through sintered frits. In this apparatus solvent can be redistilled on the grafted oxide side, and thus further washing can be carried out avoiding use of fresh solvent. Solvents were purified and dried according to standard procedures.

Elemental analyses were performed at Mikroanalytisches Labor Pascher. Gas-phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and HP5 (30 m \times 0.32 mm) or KCl/Al₂O₃ (50 m \times 0.32 mm) column for t-butanol or isobutene determination, respectively.

Diffuse reflectance infrared spectra were collected in a Nicolet 6700 FT-IR spectrophotometer in 4 cm⁻¹ resolution. An air-tight IR cell with CaF₂ window was applied and the final spectra comprise 64 scans.

Raman spectroscopy was performed on a Horiba Yvon LabRAM Aramis with a CCD-camera as a detector using a 50 \times objective, an 1800 gr/mm grating, a 100 μ m slit and a 473 nm cobalt laser. The Raman spectra were collected on the samples sealed under Ar atmosphere, which were packed in a closed cell fitted with rubber O ring and a Quartz window.

Solution NMR spectra were recorded on an Avance-300 Bruker spectrometer. All chemical shifts were measured relative to residual ¹H or ¹³C resonances in the deuterated solvent: C₆D₆, δ 7.16 ppm for ¹H, 128.06 ppm for ¹³C. ¹H and ¹³C solid-state NMR spectra were recorded on Brüker Avance-500 spectrometers with a conventional double-resonance 4 mm CP-MAS probe. The samples were introduced under argon in a zirconia rotor (4 mm), which was then tightly closed. In all experiments, the rotation frequency was set to 10 kHz. Chemical shifts were given with respect to TMS as external reference for ¹H and ¹³C NMR.

Diffuse reflectance UV-vis spectra in the range 200–800 nm were taken on a Perkin Elmer λ1050 UV-Vis-NIR Spectrophotometer adapted with the Praying Mantis optical unit provided by Harrick. The spectrum for material **1b** was recorded against BaSO₄ baseline. An airtight cell with

quartz windows was used. The UV-vis spectra were processed with Microsoft Excel software, consisting of calculation of the Kubelka-Munk function, $F(R_\infty)$, which was extracted from the UV-vis DRS data. The edge energy (E_g) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of a plot of $[F(R_{inf})hv]^{1/n}$, where $n = 0.5$ for the direct allowed transition, vs hv , where hv is the incident photon energy.^{S1-S3}

Supporting Section 2 Preparation of **1a and **1b** and proposed mechanism for the transformation of **1a** to **1b****

Preparation of **1a and **1b**:**

In a glovebox a double Schlenk is charged with $[(O=)Mo(O'Bu)_4]$ ^{S4} (912 mg, 2.25 mmol) and partially dehydroxylated silica at 200 °C SiO₂₋₂₀₀ (2.5 g). After evacuation to of the double Schlenk to 10^{-5} mbar pentane is distilled over the complex, the obtained solution is then transferred onto the silica. After 3 h reaction at room temperature, the supernatant is filtered off and the solid washed five times with pentane by reusing it doing distillation-condensation cycles. Evaporation of the volatiles and qualitative analysis of them revealed the presence of tert-butanol. Material **1a** is obtained as a slightly yellow powder after drying under vacuum (10^{-5} mbar).

Heating of **1a** under dynamic vacuum at 250 °C (2 °C·min⁻¹) gave **1b** as a pale grey powder. Condensation and analysis by gas chromatography of the volatiles revealed the release of 0.8 mol of iso-butene per Mo, tert-butanol is qualitatively observed by mass spectroscopy.

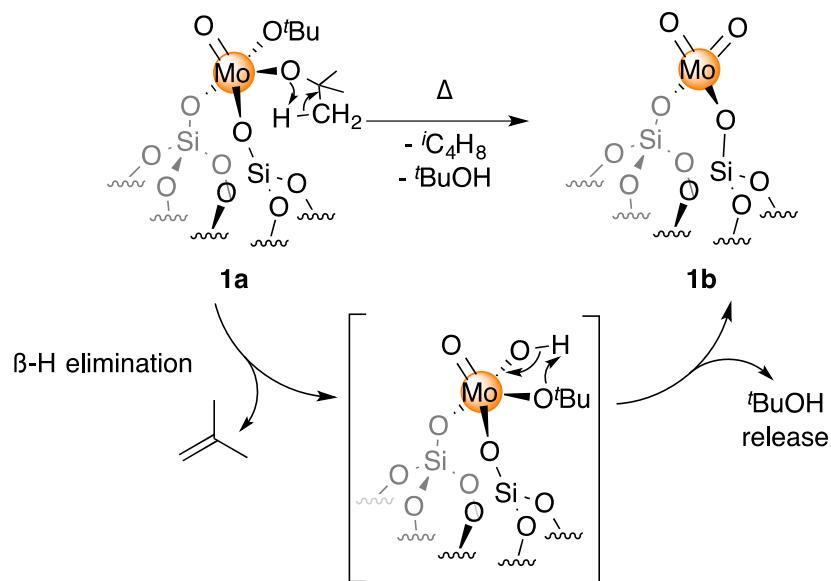


Figure S1 Proposed mechanism for the formation of the Mo bis-oxo (**1b**) from Mo mono-oxo bis tert-butoxide (**1a**) through a combination of β -H elimination and alcohol condensation.

Supporting Section 3 Raman spectrum of **1b**

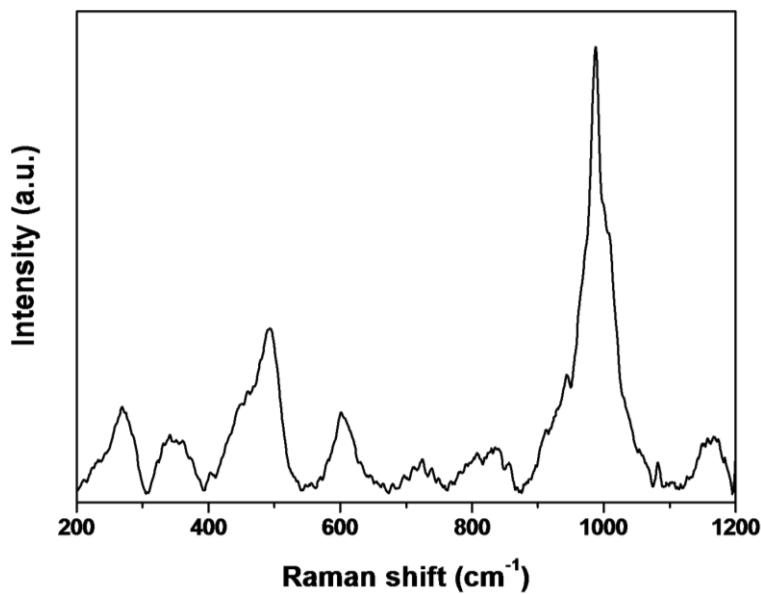


Figure S2 Raman spectrum of Mo bis-oxo species **1b**.

Supporting Section 4 UV-vis DRS Spectrum of 1b

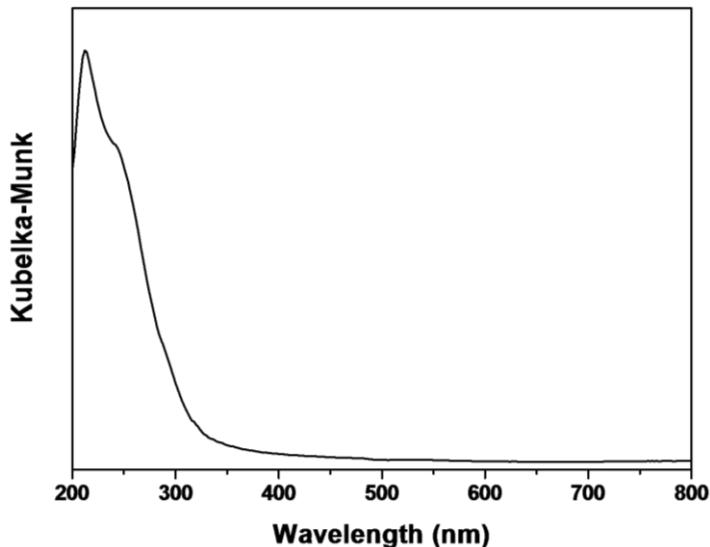


Figure S3 DR UV-Vis spectrum of **1b**.

Supporting Section 5 X-ray absorption spectroscopy

EXAFS. The spectra were acquired at ESRF, using beam-line BM23, at room temperature at the molybdenum K-edge, with a double crystal Si(111) monochromator detuned 70% to reduce the higher harmonics of the beam. The spectra were recorded in the transmission mode between 19.7 and 21.2 keV, every 0.3 eV in the edge area and every 1 eV for EXAFS. Four scans were collected for each sample. Each data set was collected simultaneously with a Mo foil reference (19999.5 eV),^{S5} and was later aligned according to that reference (maximum of the first derivative of the first peak of the Mo foil). The Mo sample was packaged within an argon filled glovebox in a double air-tight sample holder equipped with kapton windows. The data analyses were carried out using the program “Athena”^{S6} and the EXAFS fitting program “RoundMidnight”,^{S7} from the “MAX” package, using spherical waves. The program FEFF8 was used to calculate theoretical files for phases and amplitudes based on model clusters of atoms.^{S8} The scale factor, $S_0^2 = 0.68$, was evaluated from the crystallized molecular complex $\text{Mo}=(\text{O})\text{Ns}_2(\text{ONp})_2$, characterized by XRD (almost square-based pyramid with an oxo in the apical position; 1.699 Å for M=O; 1.87 Å for M-O; 2.159 Å for M-C). This sample was studied diluted in BN and conditioned as a wafer. The

refinements were carried out by fitting the structural parameters N_i , R_i , σ_i and the energy shift, ΔE_0 (the same for all shells). The fit residue, ρ (%), was calculated by the following formula:

$$\rho = \frac{\sum_k [k^3 \chi_{\text{exp}}(k) - k^3 \chi_{\text{cal}}(k)]^2}{\sum_k [k^3 \chi_{\text{exp}}(k)]^2} * 100$$

The minimization of the quality factor, $(\Delta\chi)^2/v$, (v : number of degrees of freedom in the signal), was considered in order to control the number of variable parameters in the fit, as recommended by the Standards and Criteria Committee of the International XAFS Society^{S9}

Table S1: Reported Mo=O and Mo-O bond lengths in selected bis oxo siloxy molybdenum molecular complexes.

Example	Observed distance (Å)	Reference
$[(\text{Bu}_2\text{Si(O)}_2\text{MoO}_2)_2\text{py}]$	1.694 to 1.708 Å for Mo=O and 1.871 to 1.910 Å for Mo-OSi; with Mo-N at 2.305(3) Å	Gosink, H.-G., Roesky, H. W., Noltemeyer, M., Schmidt, H.-G., Freire-Erdbrügger, C. & Sheldrick, G. M. <i>Chem. Ber.</i> 126 , 279-283 (1993).
$[\text{MoO}_2\{\text{O}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{OH}\}(\text{OSiBuPh}_2)]$	1.702 to 1.708 Å for Mo=O and 1.891(2) for Mo-OSi; with Mo-OCH ₂ - at 1.990(2) Å and Mo-O(H)CH ₂ - at 2.303(2) Å	Ma, X., Yang, Z. Ringe, A. & Magull, J. <i>Z. Anorg. Allg. Chem.</i> 633 , 1320-1322 (2007).
$[(\text{c-C}_5\text{H}_9)_7\text{Si}_7(\text{OTMS})\text{MoO}_2(\text{NC}_5\text{H}_5)]_2$	1.687 to 1.701 Å for Mo=O and 1.896 to 1.911 Å for Mo-OSi; with Mo-N at 2.283(9) Å	Fehler, F. J.; Rahimian, K.; Budzichowski, T. A. & Ziller, J. W. <i>Organometallics</i> 14 , 3920-3926 (1995)
$[\text{MoO}_2(\text{OSiPh}_3)_2(\text{PPh}_3)_x]$, with $x = 0$ or 1	1.663 to 1.699 Å for Mo=O and 1.810 to 1.928 Å for Mo-O, the shortest bond lengths being observed for the complex without coordinated phosphine	Huang, M. & DeKock, C. W. <i>Inorg. Chem.</i> 32 , 2287-2291 (1993).

Supporting Section S6 Catalysis Details

All gases were purchased from Abdul Hashim gases (AHG). Grade 5.0 helium, nitrogen and oxygen were used here, whereas propene (C_3H_6) and cis-2-butene were grade 4.0 and 3.5. All inert gases were further purified using triple filters purchased from Agilent to remove traces of water, O_2 , and hydrocarbons. C_3H_6 was further purified using molecular sieve 3 \AA and a copper based catalyst to remove water and O_2 respectively.

All catalytic tests were conducted in gas-phase using a fixed-bed isothermal flow reactor purchased from Process Integral Development and Engineering Technology[®] (*PI&DEng.&Tech.*). The flow of all gases was controlled using calibrated Bronkhorst[®] mass flow controllers. First, 75 to 200 mg of catalyst is loaded in a stainless steel reactor (length 30 cm and *I.D.* 9 mm) inside a glove box under inert atmosphere. To avoid any exposure of the catalyst to air, both ends of the tube are connected to a two positions 4-way valve that can be manually switched between two positions allowing the possibility of by-passing the reactor. Later, a gas mixture containing 6-8 v/v% olefins, 2.5-10 v/v % O_2 , 12.5 v/v % N_2 , in He (Bal.) was introduced into the reactor using a total flow rate of 32 mL/min @ NTP (16 mL/min @ NTP in case of cis-2-pentene). Propylene and butene-2 were used in the gas phase. With cis-2-pentene which is mostly liquid at room temperature was introduced into the catalytic system using a saturator bubbled with He (its flow was controlled by a calibrated Bronkhorst mass flow controllers). The control of the flow rate of cis-2-pentene was achieved by controlling the temperature of the liquid in the saturator chamber and the He flow rate. The exact molar fraction of cis-2-pentene in the total feed was evaluated by previously calibrating the GC system (through manual injection) using highly pure (analytical grade) liquid sample of cis-2-pentene.

Finally, the reactor was heated to the required temperature (350-450 °C) and the reaction was studied under steady-state conditions. On-line gas analysis of the products was performed on a Varian 450 GC gas chromatograph. A sample from the reactor outlet stream was automatically injected on three parallel channels referred to here as channel A, channel B and channel C. In Channel A, the sample (1 mL @ STP) was injected on a set of three packed columns, “*Hayesep*”[®] *Q* (CP81073), “*Hayesep*”[®] *T* (CP81072), and “*Molsieve*”[®] 13X (CP81073) connected in series. A set of 10-way and 6-way Valco[®] valves were used to allow automatic injection of the sample, back-flushing of Hayesep T, and by-passing of Molsieve 13X columns. This channel was equipped with a TCD detector (He as reference gas) and used to monitor the amount of CO and CO_2 , O_2 and N_2 . Channel B uses HP-AL/KCL column. This channel was equipped with a FID detector and used to monitor hydrocarbons. Channel C uses HP-PLOT U for the studies using propylene as substrate whereas or HP-PLOT Q was used for the studies using other olefin substrates. This channel was equipped with a FID detector and used to monitor oxygenates and some of the selected hydrocarbons.

Conversion X (expressed in %) was calculated using the following formula

$$X = \frac{(x_{N2} - x_3)}{x_{N2}} \times \frac{x_{N2}^{\circ}}{x_3^{\circ}}$$

And the carbon selectivity of carbonaceous reaction product i was assessed as follows

$$S_i = \frac{(n_i x_i)}{\sum n_i x_i}$$

Here, x°_3 and x_3 are the initial molar fractions of butene-2, propylene or pentene at the reactor inlet and outlet respectively. x°_{N2} and x_{N2} are the molar fraction of N₂ at the inlet and the outlet of the reactor resp. x_i is the molar fraction of carbonaceous product i at the reactor outlet, whereas n_i is the number of carbons in hydrocarbon i . In most of the studies, the carbon mass balance were found in the range of 94-99%. We could not get higher values of mass balance because the number of compounds analyzed.

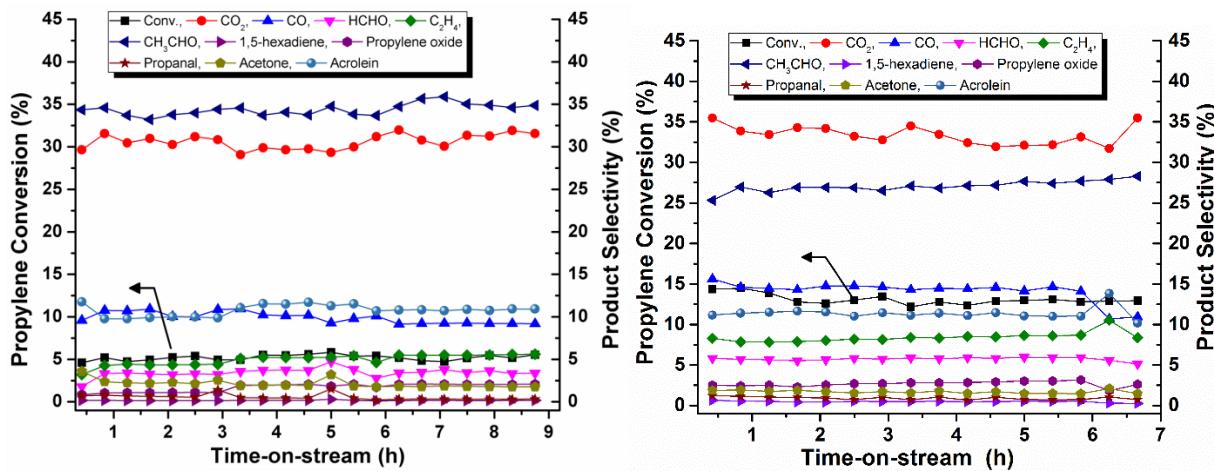


Figure S4 The plot (left) at 400 °C and (right) at 450 °C, represent conversion and selectivity vs time-on-stream for propylene oxidation over ($\equiv\text{SiO}_2\text{Mo}(\equiv\text{O})_2$) (**1b**). Reaction conditions: Cat. wt: 150 mg; Feed ratio: C₃=/O₂/N₂/He = 7.5/10/12.5/70; Total flow: 32 mL/min; Gas hourly space velocity (GHSV) of 12800 h⁻¹; W/F: 0.281 g·s·mL⁻¹.

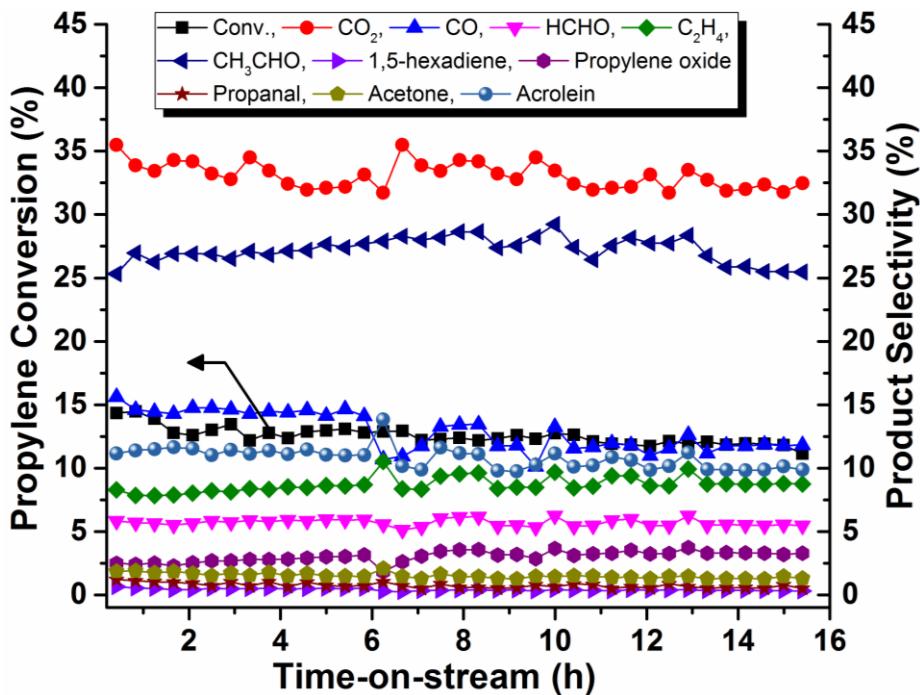


Figure S5 The conversion and selectivity vs time-on-stream plot of propylene oxidation over $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$ at $450\text{ }^\circ\text{C}$, over a prolonged experimental time of 16 h. Reaction conditions: Cat. wt: 150 mg; Feed ratio: $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2/\text{He} = 7.5/10/12.5/70$; Total flow: 32 mL/min; Gas hourly space velocity (GHSV) of 12800 h^{-1} ; W/F: $0.281\text{ g}\cdot\text{s}\cdot\text{mL}^{-1}$.

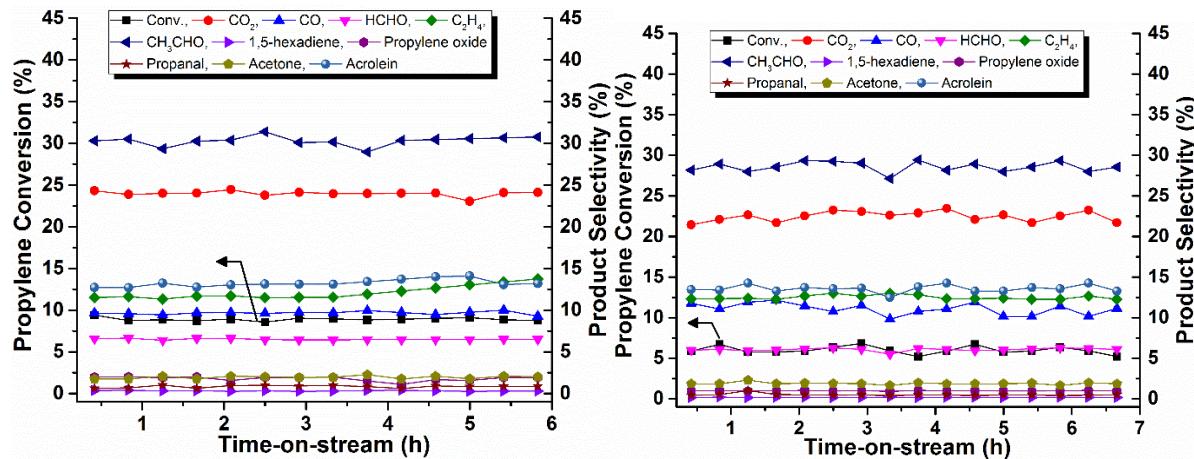
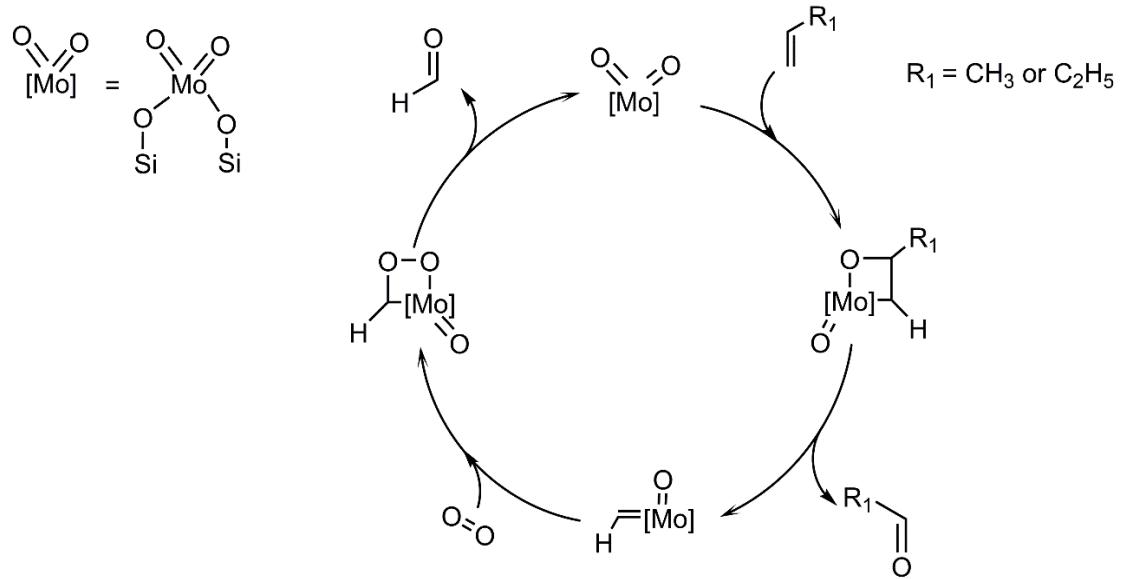


Figure S6 The conversion and selectivity vs time-on-stream plot of propylene oxidation at $450\text{ }^\circ\text{C}$ over catalyst **1b**, $(\equiv\text{Si-O-})_2\text{Mo}(=\text{O})_2$. Reaction conditions: Cat. wt: 150 mg; Feed ratio: $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2/\text{He} = 7.5/5/12.5/75$ (for left); Feed ratio: $\text{C}_3\text{H}_6/\text{O}_2/\text{N}_2/\text{He} = 7.5/2.5/12.5/77.5$ (for right); Total flow: 32 mL/min; Gas hourly space velocity (GHSV) of 12800 h^{-1} ; W/F: $0.281\text{ g}\cdot\text{s}\cdot\text{mL}^{-1}$.

(a)



(b)

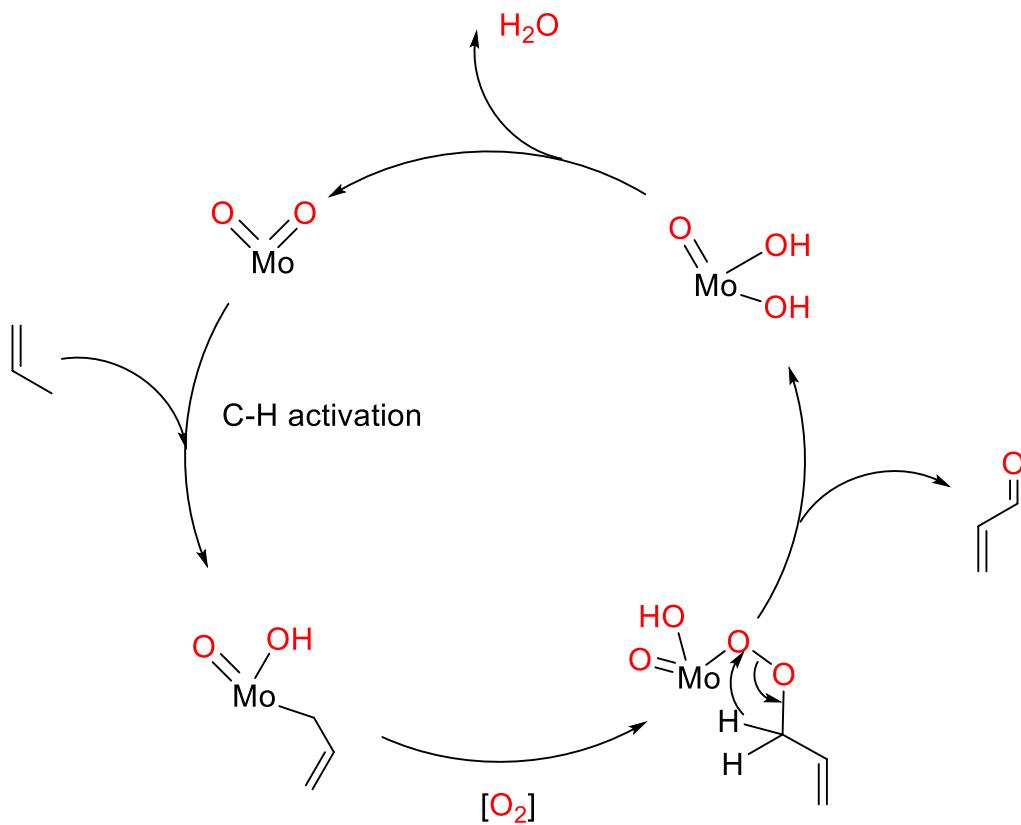


Figure S7 Proposed mechanistic pathway for the formation of formaldehyde from α -olefins (**a**) and for the formation of acrolein from alpha olefin (**b**).

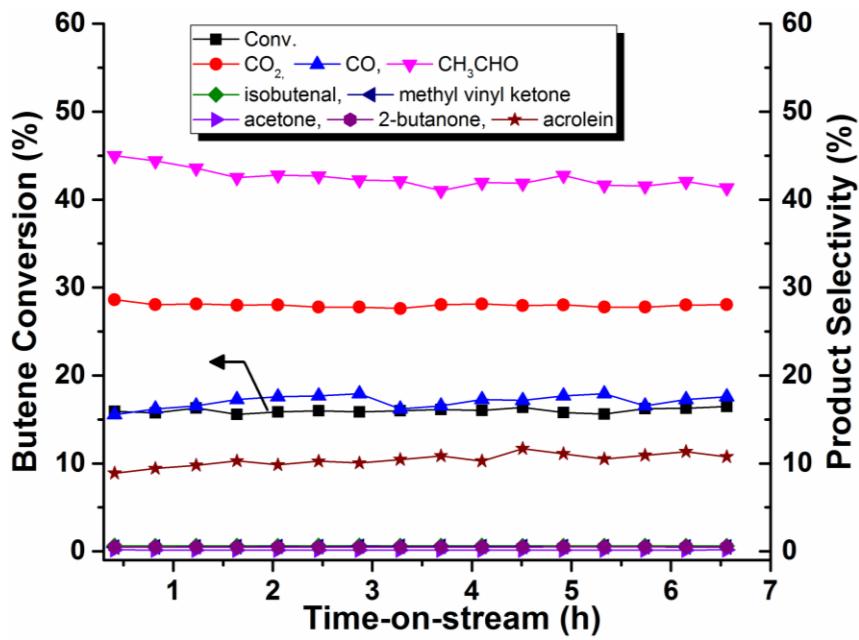


Figure S8 The conversion and selectivity vs time-on-stream plot of cis-2-butene oxidation over $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$ at 450 °C. Reaction conditions: Cat. wt: 200 mg; Feed ratio: $\text{C}_4=\text{O}_2/\text{N}_2/\text{He} = 7.5/10/12.5/70$; Total flow: 32 mL/min; Gas hourly space velocity (GHSV) of 9600 h⁻¹; W/F: 0.375 g·s·mL⁻¹.

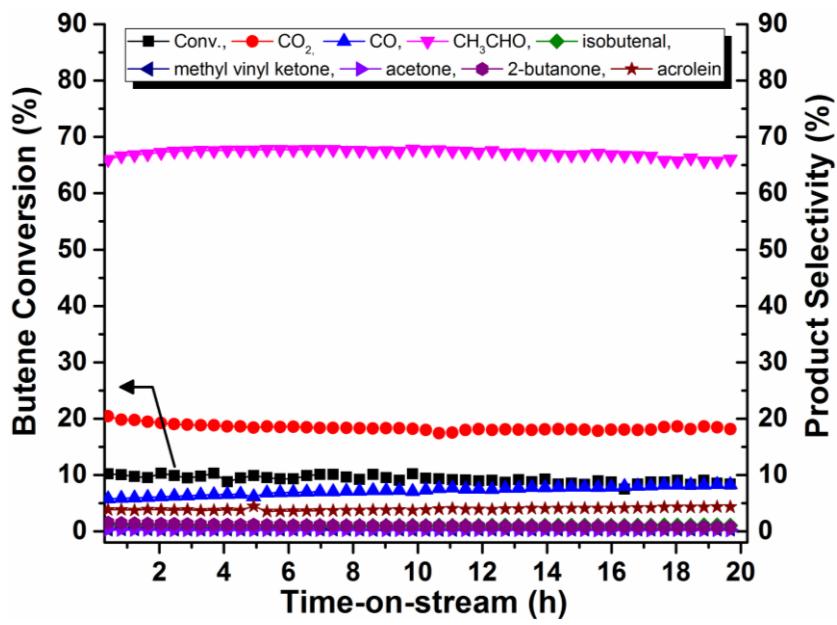


Figure S9 The conversion and selectivity vs time-on-stream plot of cis-2-butene oxidation over $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$ at 400 °C, over a long experimental time of about 20 h. Reaction conditions: Cat. wt: 200 mg; Feed ratio: $\text{C}_4=\text{O}_2/\text{N}_2/\text{He} = 7.5/10/12.5/70$; Total flow: 32 mL/min; Gas hourly space velocity (GHSV) of 9600 h⁻¹; W/F: 0.375 g·s·mL⁻¹.

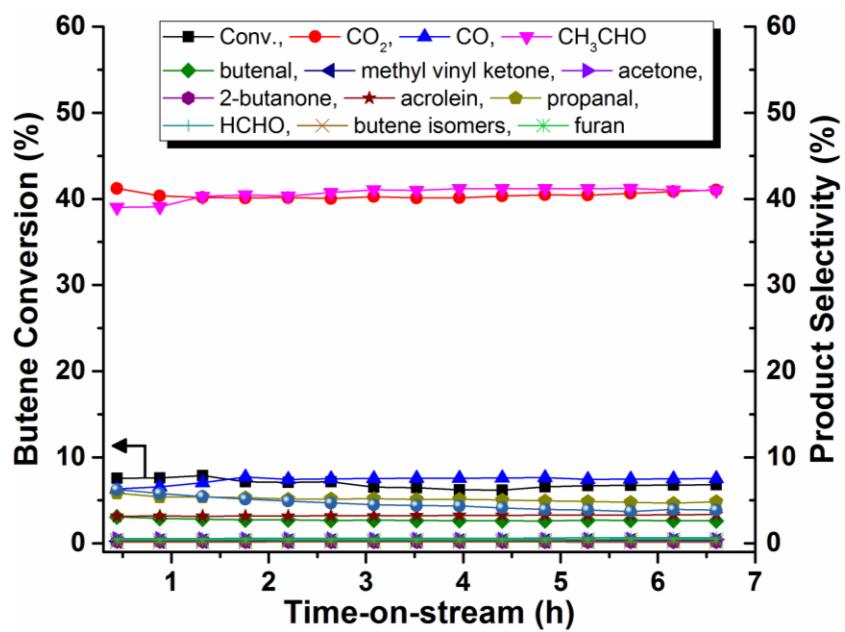


Figure S10 The conversion and selectivity vs time-on-stream plot of cis-2-pentene oxidation over $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$ at 400 °C. Reaction conditions: Cat. wt: 75 mg; Feed ratio: $\text{C}_5\text{H}_8/\text{O}_2/\text{N}_2/\text{He} = 5.9/7.8/12.5/73.8$; Total flow: 16 mL/min; Gas hourly space velocity (GHSV) of 12800 h⁻¹; W/F: 0.281 g·s·mL⁻¹.

Table S2 Summary of the catalytic oxidation results obtained with $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$ using propylene as reactant

Temp. (°C)	Feed (%) $\text{C}_4\text{H}_8, \text{O}_2, \text{N}_2, \text{He}$	Conv. $\text{C}_4\text{H}_8(\%)$	Selectivity (%)									
			CO_2	CO	Acetone	CH_3CHO	HCHO	Ethylene	Propanal	Propylene oxide	1,5-hexadiene	
400	7.5, 10, 12.5, 70	5-6	30-32	9-10	2-3	33-35	3-4	4-6	0.5	1-2	0.2	9-11
450	7.5, 10, 12.5, 70	12-14	31-34	11-14	1-2	25-29	5-6	8-9	0.5-1	3	0.4	9-12
450	7.5, 5, 12.5, 75	9-9.5	23-24	9-10	2	30-31	6-6.5	11-13	0.5-1	1-2	0.4	13-14
450	7.5, 2.5, 12.5, 77.5	5-6	21-23	10-11	2	28-29	6	12.5	0.5	1	0.2	10-11

Table S3 Summary of the catalytic oxidation results obtained with $(\equiv\text{SiO})_2\text{Mo}(=\text{O})_2$ using cis-2-butene as reactant

Temp. (°C)	Feed (%) $\text{C}_4\text{H}_8, \text{O}_2, \text{N}_2, \text{He}$	Conv. $\text{C}_4\text{H}_8(\%)$	Selectivity (%)							
			CO_2	CO	Acetone	CH_3CHO	Isobutenal	Methyl vinyl ketone	2-butanone	Acrolein
350	7.5, 10, 12.5, 70	5	12-14	2-3	0.5	71	0.5	2	2-3	3-4
400	7.5, 10, 12.5, 70	9-10	17-20	6-8	0.3	66-68	0.4	1	1-1.5	3-4
450	7.5, 10, 12.5, 70	15-16	27-28	15-17	0.15	41-44	0.6	0.6	0.5-1	10-11

Table S4 Summary of the catalytic oxidation results obtained with $[(\equiv \text{SiO})_2\text{Mo}(=\text{O})_2]$ (**1b**) using cis-2-pentene as reactant

Temp. (°C)	Feed (%) $\text{C}_{5\text{-}}\text{O}_2, \text{N}_2, \text{He}$	Conv. $\text{C}_{5\text{-}}\text{(%)}$	Selectivity (%)										
			CO_2	CO	Acetone	CH_3CHO	Isobutenal	Methyl vinyl ketone	2-butanone/HCHO	Butenes	Furan	Acrolein	Propanal
400	5.9, 7.8, 12.5, 73.8	7	40	7	0.5	40-41	2.6	0.3	0.2/0.6	0.2	0.4	3	5

Supporting Section 7 Computational details

Geometry optimizations and calculations of thermochemical corrections. All geometry optimizations were performed with the PBE GGAS10^{S10} DFT functional as implemented in PRIRODA 13 electronic structure code.^{S11} All electron basis sets ($\lambda 1$)^{S12} of valence double- ζ plus polarization quality were used. All stationary molecular geometries were characterized by analytically calculated matrix of electronic energy second derivatives with respect to nuclear coordinates (Hessian). No imaginary frequencies have been found for all reactants, products and intermediates. Only one imaginary frequency have been detected for all transitions states. Possible relativistic effects (for molybdenum) were taken into account via the scalar Dyall Hamiltonian.^{S13}

The default, adaptively generated PRIRODA grid, corresponding to an accuracy of the exchange-correlation energy per atom (1×10^{-8} Hartree) was decreased by a factor of 100 for more accurate evaluation of the exchange-correlation energy term. Default values were used for the Self-Consistent-Field (SCF) convergence and the maximum gradient for geometry optimization criterion (1×10^{-4} au), whereas the maximum displacement geometry convergence criterion was decreased to 0.0018 au.

Translational, rotational, and vibrational partition functions for thermal corrections to arrive at total Gibbs free energies were computed within the ideal-gas, rigid-rotor, and harmonic oscillator approximations. The temperature used in the calculations of thermochemical corrections was set to 298.15 K in all the cases.

Single-point (SP) energy evaluations. The energies were re-evaluated in Single-Point fashion at optimized geometries by means M06^{S14} functional as implemented in Gaussian 09^{S15} code. The all-electron def2-tzvpp basis sets of Ahlrichs^{S16} were used on all main-group elements. On molybdenum atom the Stuttgart ECP^{S17} was used with the corresponding valence def2-tzvpp basis set. The “Integral(grid=ultrafine)” option was used for evaluation of the exchange-correlation term. The default value for the SP SCF convergence was adopted.

Silica model. A relatively large cluster model cut out from the β -cristobalite-based SiO_2 surface (model 001-4 in the paper) published by Rozanska et al.^{S18} has been chosen to simulate a silica surface, see Figure S11.

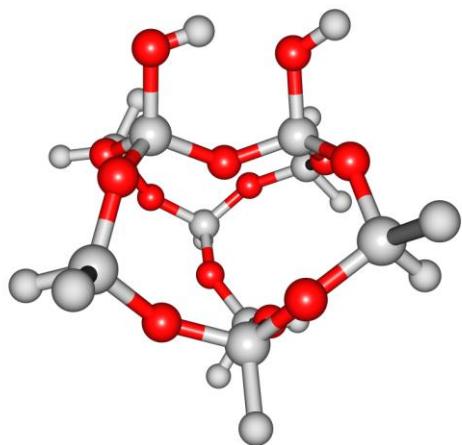


Figure S11 The silica cluster model used in the present work. Color coding: Si (gray), O (red), H (gray).

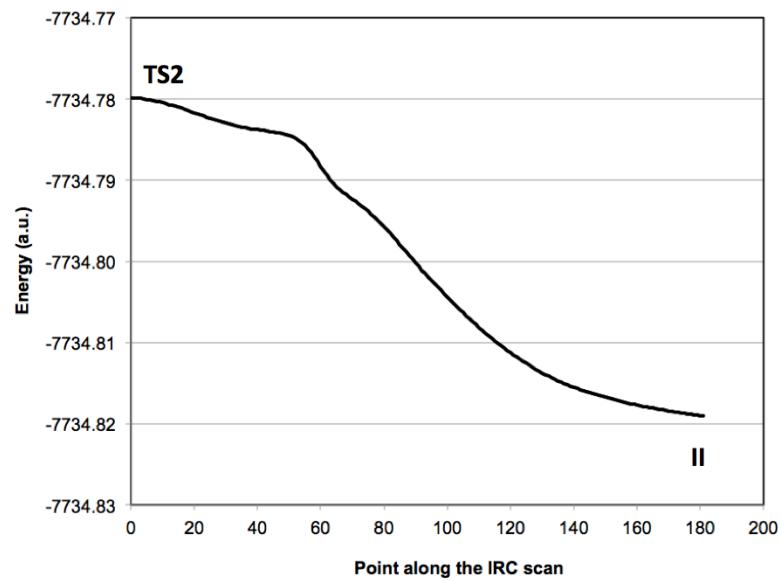


Figure S12 Intrinsic reaction coordinate plot showing the connection between transition state **TS2**, presenting a large C-C distance of 2.86 Å, and the preceding intermediate **II**.

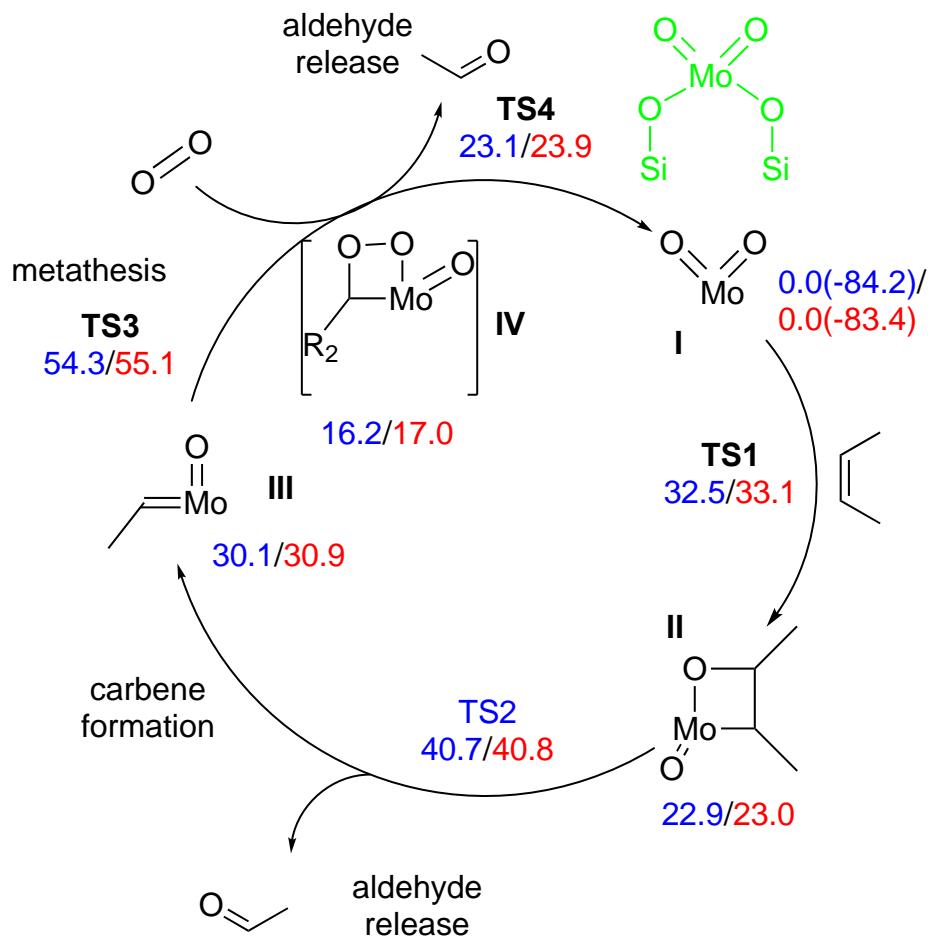


Figure S13. Comparison of the reaction pathways for oxidation of cis and trans 2-butene to acetaldehyde by O_2 and catalyzed by a model of $(\equiv Si-O)^2 Mo(=O)_2$. The DFT-calculated ΔG (kcal/mol) values are reported in blue/red for cis/trans butane, near the structure labels.

Energies and Cartesian coordinates (\AA) of the individual compounds.

C₂H₄O

Charge of molecule: 0
 Multiplicity: 1
 E (PBE/L1, Priroda)= -153.77858948 (a.u.)
 Gibbs free energy correction = 0.0288610721571 (a.u.)
 E (MO6/def2-tzvpp, gas, G09)= -153.795135095 (a.u.)

O	0.30793822	0.79022994	-1.64652064
C	-0.00170146	0.71136797	-0.48000765
H	-0.33721794	1.61846145	0.09620091
C	0.01081088	-0.55339738	0.33942050
H	-0.99964712	-0.73863820	0.74416341
H	0.34334884	-1.40954793	-0.26341308
H	0.67646858	-0.41847584	1.21015656

C4H8_cis

Charge of molecule: 0

Multiplicity: 1

E (PBE/L1, Priroda)= -157.10514780 (a.u.)

Gibbs free energy correction = 0.0771304500255 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -157.147466797 (a.u.)

C	0.05156732	0.78417032	-0.66847749
C	-0.05160540	0.78416729	0.66847924
H	0.09134473	1.75960192	-1.16959524
H	-0.09141160	1.75959577	1.16959211
C	-0.12305001	-0.40432674	1.58249939
H	-1.05635400	-0.38854923	2.17295429
H	-0.08234116	-1.36118387	1.04223650
H	0.70699399	-0.38971038	2.31084786
C	0.12308677	-0.40430383	-1.58252079
H	1.05645586	-0.38864776	-2.17286412
H	0.08225952	-1.36117190	-1.04227436
H	-0.70694602	-0.38964158	-2.31087739

III

Charge of molecule: 0

Multiplicity: 1

E (PBE/L1, Priroda)= -7580.99684160 (a.u.)

Gibbs free energy correction = 0.124636824324 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -3596.20997937 (a.u.)

Si	1.10819371	0.02448638	2.33889821
O	2.45775047	0.79478685	1.76265100
Si	3.30630798	1.50554839	0.52453326
O	0.88709744	-1.45691301	1.60101488
Si	1.03115211	-2.36436699	0.20708134
O	-0.22235628	1.03682343	2.15118761
Si	-0.87849963	1.48040217	0.69373647
O	-0.29300473	2.90362417	0.08545604
Si	0.95625674	3.03713451	-1.03384902
O	0.69441958	2.12480540	-2.40519324
Si	0.87972618	0.65134659	-3.16416339
O	2.29512849	-0.08266858	-2.70326956
Si	3.23157061	-0.80776968	-1.54120605
O	3.86245238	0.34114515	-0.52116708
O	2.36811723	-1.92678697	-0.66914346
O	-0.32917060	-2.24571700	-0.77627844
Si	-0.95147008	-0.82466063	-1.36289990
O	-0.39758758	-0.40207065	-2.86391261
O	-2.52485683	1.45065846	0.70356552
O	-0.29993816	0.32668743	-0.35512280
O	2.38055941	2.61165407	-0.29568935
O	-2.59545421	-0.76895560	-1.28171198
H	1.15495247	-3.78140813	0.60465291
H	4.35163544	-1.50231966	-2.20772745
H	4.47161276	2.20591306	1.10137483
H	1.02743320	4.45604922	-1.43565670
H	1.26874883	-0.21493868	3.78745103

H	0.91208115	0.88820779	-4.62109424
Mo	-3.75061928	0.14756776	-0.03098462
O	-5.27256517	0.65148626	-0.53565356
C	-4.16232043	-1.07491748	1.35365767
H	-5.21691995	-1.26284825	1.60557463
C	-3.13347573	-1.82339328	2.15209993
H	-3.24010124	-1.58436476	3.22688826
H	-3.28401016	-2.91340484	2.03928625
H	-2.09284612	-1.60082293	1.86561358

II_cis

Charge of molecule: 0

Multiplicity: 1

E (PBE/L1, Priroda)= -7734.82103128 (a.u.)

Gibbs free energy correction = 0.181301472463 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -3750.04437375 (a.u.)

Si	1.98747428	0.65987340	2.03545243
O	3.22042263	1.52020192	1.33729800
Si	3.91966914	2.25121465	0.01954697
O	1.87388267	-0.87687445	1.39313645
Si	2.02653886	-1.82896687	0.03004420
O	0.55570794	1.53458738	1.87710118
Si	-0.19023032	1.82295206	0.42568548
O	0.18173786	3.27419131	-0.27461847
Si	1.35255571	3.47204064	-1.47039371
O	1.11548074	2.47254419	-2.78425442
Si	1.38689371	0.97748403	-3.47329863
O	2.88547211	0.39208568	-3.06342280
Si	3.95658145	-0.16479434	-1.92518938
O	4.52739252	1.09871868	-1.01055557
O	3.26768787	-1.30922499	-0.93766854
O	0.61070333	-1.88642414	-0.88015137
Si	-0.16362612	-0.54713480	-1.47804056
O	0.23046190	-0.16741000	-3.03977501
O	-1.81936388	1.57373288	0.49967021
O	0.49036149	0.69974822	-0.59143889
O	2.84505302	3.22424932	-0.78767930
O	-1.78964882	-0.58594691	-1.25523587
H	2.30582521	-3.20931146	0.47563594
H	5.10021827	-0.78483219	-2.62458458
H	5.04176185	3.08597285	0.49433444
H	1.26052422	4.86953131	-1.93703582
H	2.24916654	0.52318392	3.48256185
H	1.31495474	1.13198908	-4.93969545
Mo	-3.09296670	0.27631564	-0.12384615
O	-4.22324704	0.78470254	-1.26959607
O	-4.11850760	0.19934214	1.46793588
C	-3.52573681	-1.78334023	0.57172642
C	-4.05902540	-1.20479534	1.88301892
H	-4.37249925	-2.06112371	-0.08289530
H	-5.09671637	-1.51750807	2.11501563
C	-2.47849548	-2.87857335	0.59126683
H	-1.56501683	-2.59093645	1.13644380
H	-2.87973573	-3.78726470	1.07966539

H -2.18013023 -3.15861174 -0.42908404
 C -3.19761371 -1.34870111 3.12551589
 H -3.61394066 -0.73548453 3.93971674
 H -3.17809253 -2.39939057 3.45608922
 H -2.16193456 -1.01801191 2.94159808

TS1_cis

Charge of molecule: 0

Multiplicity: 1

E (PBE/L1, Priroda)= -7734.80917216 (a.u.)

Gibbs free energy correction = 0.179443364355 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -3750.02723313 (a.u.)

Si 2.52620770 0.90200007 2.18815805
 O 3.64726665 1.80355397 1.36194094
 Si 4.18252803 2.51953984 -0.03791377
 O 2.44757972 -0.66009816 1.60763782
 Si 2.51315149 -1.64603621 0.26049357
 O 1.04250133 1.70136746 2.12398680
 Si 0.17874813 1.88583572 0.72330160
 O 0.37916510 3.33867380 -0.04348256
 Si 1.43779243 3.55983370 -1.33740078
 O 1.14777429 2.51416342 -2.60359083
 Si 1.42894820 1.00265284 -3.25556980
 O 2.98670516 0.50546630 -2.96538158
 Si 4.17619651 0.04116657 -1.90580477
 O 4.75514482 1.36387938 -1.08381715
 O 3.64072093 -1.10396117 -0.82950040
 O 1.02997242 -1.79924515 -0.51694790
 Si 0.14335605 -0.50834861 -1.07497692
 O 0.37138285 -0.17384250 -2.68414842
 O -1.42195185 1.52647588 0.93973252
 O 0.86778818 0.78973665 -0.31505310
 O 2.99192877 3.41304672 -0.77245379
 O -1.43194658 -0.624443976 -0.67300121
 H 2.90144049 -2.99601622 0.71851796
 H 5.28907474 -0.54084394 -2.68393260
 H 5.29692908 3.42656663 0.30519227
 H 1.23322353 4.93645452 -1.83063100
 H 2.91522081 0.83436324 3.61126123
 H 1.22295227 1.10004526 -4.71478226
 Mo -2.79336766 0.27338174 0.43844045
 O -3.90941334 1.08027294 -0.54108913
 O -3.54913130 -0.07830900 2.04287491
 C -3.80376073 -1.75536285 0.15493066
 C -4.53144811 -1.38310620 1.36681279
 H -4.37540900 -1.59582289 -0.76921799
 H -5.45278127 -0.81033678 1.19371275
 C -2.93051795 -2.99048963 0.13743266
 H -2.20832760 -3.01774656 0.97034355
 H -3.53501644 -3.91463782 0.18676391
 H -2.34875563 -3.01840179 -0.79498656
 C -4.59293144 -2.29360411 2.55915527
 H -5.01100304 -1.76928950 3.42932669
 H -5.25381214 -3.14030915 2.29813782

H -3.60412559 -2.69822865 2.81552830

TS2_cis

Charge of molecule: 0

Multiplicity: 1

E (PBE/L1, Priroda)= -7734.77988573 (a.u.)

Gibbs free energy correction = 0.173837805966 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -3750.00861645 (a.u.)

Si	2.59153351	0.03191881	1.74262067
O	3.58255733	1.23466082	1.17207805
Si	3.96611838	2.34671494	0.00004461
O	2.66658360	-1.32979430	0.78133109
Si	2.79110280	-1.92264343	-0.77608720
O	1.03286823	0.64174080	1.90750980
Si	0.06448715	1.05226924	0.62078760
O	0.08738576	2.66870692	0.24176756
Si	1.06479716	3.33447074	-0.95468113
O	0.85156742	2.62597783	-2.44940407
Si	1.27973728	1.37833617	-3.47375457
O	2.89737365	1.02335059	-3.33903555
Si	4.16991554	0.44863475	-2.44403452
O	4.62836673	1.57932553	-1.31543947
O	3.81074485	-0.98745835	-1.69360974
O	1.31105451	-2.05414064	-1.55737955
Si	0.24810375	-0.78976614	-1.75312953
O	0.39187284	-0.02384399	-3.22044482
O	-1.44636877	0.44621674	0.79880835
O	0.82785848	0.34871429	-0.67925006
O	2.64869314	3.24270870	-0.46243847
O	-1.28504414	-1.21078414	-1.40143818
H	3.35402840	-3.28610879	-0.68319815
H	5.31178059	0.22110006	-3.35408536
H	4.98035981	3.26757833	0.55433961
H	0.68829081	4.75793253	-1.07611808
H	3.04535143	-0.35470197	3.09518979
H	1.00744313	1.82458627	-4.85543053
Mo	-2.73473242	-0.62975156	-0.22118103
O	-3.94648817	-0.40765063	-1.37532665
O	-4.04989821	0.63859683	1.15192136
C	-3.15577956	-2.30372118	0.61277167
C	-4.78114467	-0.21260325	1.69077792
H	-4.00974962	-2.89272228	0.24296696
H	-5.48663799	-0.81534597	1.07653342
C	-2.32944752	-2.93506954	1.69461254
H	-1.56111584	-2.26054838	2.10582421
H	-2.95621393	-3.30160493	2.52909967
H	-1.80657280	-3.81871997	1.27805848
C	-4.89155462	-0.36594644	3.17126559
H	-5.85519739	0.07832852	3.48649721
H	-4.93738490	-1.43271001	3.44359333
H	-4.06664575	0.14376648	3.68706715

Charge of molecule: 0

Multiplicity: 1

E (PBE/L1, Priroda)= -7731.38712263 (a.u.)

Gibbs free energy correction = 0.130291146099 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -3746.56588229 (a.u.)

Multiplicity: 3

E(MO6/def2-tzvpp, gas, G09)= -3746.51154201 (a.u.)

Si	1.34912280	-0.27579949	2.19567567
O	2.67655383	0.58491706	1.70345183
Si	3.52007484	1.42072809	0.54125478
O	1.20209862	-1.71254278	1.36031243
Si	1.41748066	-2.51117362	-0.09043775
O	-0.01736483	0.70167053	2.04027974
Si	-0.62835427	1.20620395	0.58578777
O	-0.12398610	2.70334683	0.09957939
Si	1.15072294	2.97055943	-0.97144326
O	0.96872816	2.14926549	-2.41161297
Si	1.21883881	0.73706518	-3.26293893
O	2.63817892	0.00507785	-2.81351419
Si	3.58500053	-0.74845705	-1.67728473
O	4.14346938	0.36148110	-0.57517122
O	2.75878770	-1.95597526	-0.89071778
O	0.08222486	-2.36703901	-1.11008225
Si	-0.55720896	-0.92071069	-1.59513031
O	-0.03475140	-0.37377612	-3.06402007
O	-2.26797220	1.06612300	0.49476711
O	0.06897504	0.17054728	-0.51063840
O	2.56631794	2.54895937	-0.21541402
O	-2.20756037	-0.89862935	-1.48433666
H	1.58320465	-3.94803282	0.20424068
H	4.74657072	-1.34940968	-2.36288076
H	4.64254567	2.12152535	1.19662792
H	1.16985699	4.41640368	-1.26786786
H	1.48082227	-0.59838901	3.63070714
H	1.27606517	1.07188928	-4.69919055
Mo	-3.53966342	-0.07902175	-0.38072389
O	-4.51869275	1.05370413	-1.15962679
C	-4.14212838	-0.64315847	1.64295178
H	-5.02398410	-0.02933892	1.92009142
O	-4.69711833	-1.61979278	-0.25050275
O	-4.60252766	-1.94834827	1.18899831
C	-3.15633407	-0.79836441	2.77176079
H	-3.62121351	-1.35564473	3.60575041
H	-2.25166819	-1.34601864	2.46227062
H	-2.85511196	0.19015523	3.14902734

TS4

Charge of molecule: 0

Multiplicity: 1

E (PBE/L1, Priroda)= -7731.38383474 (a.u.)

Gibbs free energy correction = 0.129639055329 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -3746.55425377 (a.u.)

Multiplicity: 3

E(MO6/def2-tzvpp, gas, G09)= -3746.51314595 (a.u.)

Si	1.41182627	-0.31116607	2.20579956
O	2.73240949	0.54281946	1.68301155
Si	3.56865079	1.34654835	0.49355866
O	1.26364260	-1.76800374	1.40544316
Si	1.44506589	-2.58969057	-0.03665932
O	0.03992007	0.65660333	2.04947258
Si	-0.57590618	1.14240446	0.58505946
O	-0.06630495	2.63394385	0.08041544
Si	1.19031247	2.87932008	-1.01519383
O	0.98600112	2.03934103	-2.44244923
Si	1.21470442	0.60530331	-3.26363722
O	2.63941486	-0.12239238	-2.82215842
Si	3.59482335	-0.86419714	-1.68551255
O	4.17206341	0.25942728	-0.60710864
O	2.77510117	-2.05832303	-0.87236896
O	0.09322271	-2.45459923	-1.03535203
Si	-0.53345457	-1.00527622	-1.53022509
O	-0.04031888	-0.49558710	-3.02411226
O	-2.20386792	0.97645601	0.50360392
O	0.14613232	0.09634048	-0.49014094
O	2.61889788	2.46912479	-0.27590247
O	-2.17865213	-0.95917141	-1.38673191
H	1.60822381	-4.02289156	0.27773308
H	4.74634749	-1.48019501	-2.37519810
H	4.70487576	2.05022983	1.12222021
H	1.20942890	4.32036159	-1.33542199
H	1.56301905	-0.60474959	3.64560296
H	1.25224606	0.90870504	-4.70777915
Mo	-3.57069834	-0.12532083	-0.36243466
O	-4.40235950	1.03029211	-1.26543044
C	-4.31142544	-0.51678134	1.68313386
H	-5.36217475	-0.21513977	1.85551996
O	-4.78245106	-1.56162316	-0.43149849
O	-4.21011761	-1.79890022	1.14177434
C	-3.35918091	-0.29928168	2.83428189
H	-3.73107197	-0.82834935	3.72881083
H	-2.34168202	-0.65371810	2.61690939
H	-3.30666367	0.77813651	3.05296487

|

Charge of molecule: 0

Multiplicity: 1

E (PBE/L1, Priroda)= -7577.73562819 (a.u.)

Gibbs free energy correction = 0.0783278620602 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -3592.90763569 (a.u.)

Multiplicity: 3

E(MO6/def2-tzvpp, gas, G09)= -3592.77090920 (a.u.)

Si	0.64413082	-0.32949072	2.71802218
O	1.96443013	0.46596013	2.10787834
Si	2.76165992	1.20822473	0.85432396
O	0.42254244	-1.80017410	1.96423343
Si	0.54711104	-2.70016368	0.56610159

O -0.70027511 0.67924874 2.57044808
 Si -1.39255053 1.11770870 1.13732941
 O -0.88092484 2.55741818 0.51235569
 Si 0.34722210 2.72213980 -0.63303447
 O 0.05954444 1.81550275 -2.00274669
 Si 0.25086253 0.35421925 -2.78290654
 O 1.67711659 -0.37418147 -2.35575744
 Si 2.66783812 -1.08852306 -1.23052305
 O 3.30544887 0.06891914 -0.22463491
 O 1.85419968 -2.22798178 -0.33758321
 O -0.83428977 -2.58931283 -0.39601557
 Si -1.48584402 -1.17517822 -0.94441982
 O -1.01357849 -0.71489717 -2.45776183
 O -3.05034829 1.03683110 1.20890106
 O -0.84530341 -0.01568953 0.05544851
 O 1.78583526 2.30356283 0.07571464
 O -3.13995633 -1.16350318 -0.79091464
 H 0.69674783 -4.11916731 0.94230313
 H 3.77788356 -1.75526894 -1.93960843
 H 3.92840030 1.92778250 1.40253602
 H 0.38615082 4.14548110 -1.02057266
 H 0.84168195 -0.57541761 4.15955231
 H 0.24236455 0.60176839 -4.23763272
 Mo -4.27377801 -0.10254855 0.30490574
 O -5.38605225 0.78129886 -0.61757509
 O -5.15826989 -1.05456804 1.39163297

TS3

Charge of molecule: 0
 Multiplicity: 3
 E (PBE/L1, Priroda)= -7731.32891392 (a.u.)
 Gibbs free energy correction = 0.126448559408 (a.u.)
 E(MO6/def2-tzvpp, gas, G09)= -3746.50136047 (a.u.)
 Multiplicity: 1
 E(MO6/def2-tzvpp, gas, G09)= -3746.46571146 (a.u.)

Si 1.71812728 -0.05571221 2.35603284
 O 2.99798013 0.80078348 1.74034079
 Si 3.74073612 1.59938656 0.48784253
 O 1.55513693 -1.53599457 1.60172941
 Si 1.68183400 -2.38702341 0.17082173
 O 0.32958013 0.89114733 2.24939434
 Si -0.38630691 1.30945027 0.81291552
 O 0.05021481 2.79768325 0.23047981
 Si 1.24783027 3.03999142 -0.92825863
 O 0.99155593 2.16071870 -2.32302011
 Si 1.20156016 0.70676716 -3.11437589
 O 2.66414261 0.01942752 -2.73512253
 Si 3.70049126 -0.66389449 -1.63385177
 O 4.31090299 0.50474055 -0.62360205
 O 2.96006048 -1.85227321 -0.74075911
 O 0.28162519 -2.31274605 -0.76108099
 Si -0.42533523 -0.89457345 -1.24932657
 O -0.01841072 -0.40504079 -2.77940446
 O -2.01503494 1.10463605 0.86677114

O 0.29091627 0.25107466 -0.27803848
 O 2.71963922 2.67944067 -0.25021587
 O -2.05005327 -0.92041811 -1.00026784
 H 1.89567446 -3.80786145 0.51343220
 H 4.82664925 -1.27279823 -2.37073146
 H 4.89194620 2.34678929 1.03387051
 H 1.22182617 4.47238144 -1.28567610
 H 1.95448004 -0.30959084 3.79197434
 H 1.15707757 0.97252485 -4.56615595
 Mo -3.40397866 0.16721007 -0.11756000
 O -4.29615917 1.43565875 -0.76817217
 C -4.45601401 -0.51308005 1.42595235
 H -5.37871347 0.01959954 1.70070908
 O -5.45367411 -1.64126257 -0.25098122
 O -4.64055177 -1.28893439 -1.21465557
 C -4.05201317 -1.64671450 2.30528357
 H -4.90697853 -2.28508305 2.58658528
 H -3.25712889 -2.27728585 1.87496275
 H -3.64963462 -1.20912434 3.24215861

O2

Charge of molecule: 0

Multiplicity: 3

E (PBE/L1, Priroda)= -150.33515241 (a.u.)

Gibbs free energy correction = -0.0163162927078 (a.u.)

E(MO6/def2-tzvpp, gas, G09)= -150.311683017 (a.u.)

O -0.11622645 -0.25246036 0.55179918
 O 0.11622645 0.25246036 -0.55179918

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