Dioxygen activation routes in Mars-van Krevelen redox cycles catalyzed by metal oxides

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Abstract

Catalytic redox cycles involve dioxygen activation via peroxo (OO$^\cdot$) or H$_2$O$_2$ species, denoted as inner- and outer-sphere routes respectively, for metal-oxo catalysts solvated by liquids. O$_2$ activation is typically more facile than the reduction part of redox cycles, making kinetic inquiries difficult at steady-state. These steps are examined here for oxidative alkanol dehydrogenation (ODH) by scavenging OO$^\cdot$ species with C$_3$H$_6$ to form epoxides and by energies and barriers from density functional theory. Alkanols react with O-atoms (O$^\cdot$) in oxides to form vicinal OH pairs that eliminate H$_2$O to form OO$^\cdot$ at O-vacancies formed or react with O$_2$ to give H$_2$O$_2$. OO$^\cdot$ reacts with alkanols to re-form O$^\cdot$ via steps favored over OO$^\cdot$ migrations, otherwise required to oxidize non-vicinal vacancies. C$_3$H$_6$ epoxidizes by reaction with OO$^\cdot$ with rates that increase with C$_3$H$_6$ pressure, but reach constant values as all OO$^\cdot$ species react with C$_3$H$_6$ at high C$_3$H$_6$/alkanol ratios. Asymptotic epoxidation/ODH rate ratios are smaller than unity, because outer-sphere routes that shuttle O-atoms via H$_2$O$_2$(g) are favored over endoergic vacancy formation required for inner-sphere routes. The relative contributions of these two routes are influenced by H$_2$O, because vacancies, required to form OO$^\cdot$, react with H$_2$O to form OH pairs and H$_2$O$_2$. OO$^\cdot$-mediated routes and epoxidation become favored at low coverages of reduced centers, prevalent for less reactive alkanols and lower alkanol/O$_2$ ratios, because H$_2$O$_2$ then reacts preferentially with O$^\cdot$ (forming OO$^\cdot$), instead of vacancies (forming O$^\cdot$/H$_2$O). These re-oxidation routes prefer molecular donor (H$_2$O$_2$) or acceptor (alkanol) to perform stepwise two-electron oxidations by dioxygen, instead of kinetically demanding O-atom migrations. The quantitative descriptions, derived from theory and experiment on Mo-based polyoxometalate clusters with known structures, bring together the dioxygen chemistry in liquid-phase oxidations, including electro-catalysis and monooxygenase enzymes, and oxide surfaces into a common framework, while suggesting a practical process for epoxidation by kinetically coupling with ODH reaction.

1. Introduction

The oxidative dehydrogenation (ODH) and the selective oxidation or epoxidation of organic molecules provide essential routes to convert undervalued streams into marketable chemicals of higher values [1,2]. ODH reactions proceed via Mars-van Krevelen catalytic cycles on reducible metal oxides; these cycles couple the reduction and the re-oxidation of the oxide catalyst via sequences such as the one depicted in Scheme 1 [3,4]. The reduction part involves the abstraction of H-atoms from organic substrates by lattice O-atoms (O$^\cdot$) and typically limits ODH turnover rates for alkane [4–7] and alkanol [8,9] reactants. These reduction steps form two-electron reduced centers consisting of vicinal hydroxyl groups (H/ OH$^\cdot$), which can dehydroxylate and lead to reduced centers in the form of O-vacancies ($^\cdot$) in the oxide lattice; both types of reduced centers can react with O$_2$ to re-form oxidized centers (O$^\cdot$), thus completing a catalytic turnover. Re-oxidation steps are fast and thus kinetically-irrelevant in most catalytic oxidations, but can influence the selectivity of these reactions, because O$_2$-derived intermediates formed during re-oxidation steps can react with organic reactants or products to form undesired side products [10,11]. They are also of fundamental interest in electro-catalysis [12–14] and monooxygenase enzyme systems [15–18].
which use activated forms of O₂-derived species in the epoxidation of alkenes and the selective oxidation of alkanes.

The fast nature of these re-oxidation pathways renders their dynamics inaccessible to direct experimental inquiry from the kinetic behavior of steady-state ODH catalysis [3]. Re-oxidation rate constants can be indirectly probed through their in-situ UV-visible spectra during the transient formation and consumption of reduced centers in response to changes in oxidant ratios in the reactant streams [19]. Previous studies of propane visible spectra during the transient formation and consumption tent with the observed insensitivity of ODH rates to O₂ pressure [5–9]. The low surface densities of two-electron reduced centers [19] and their energetically-unfavorable pairing [11] lead to the isolation of such centers during ODH reactions. Their re-oxidation by a four-electron oxidant such as O₂ thus requires the kinetic coupling of two elementary events, each involving one O-atom (and two electrons). Such coupling requires, in turn, the migration of one of the O-atoms in O₂ or via lattice diffusion or via molecular carriers, to react with another reduced center or the decomposition of the O₂-derived species via reactions with gas-phase reductants, a requirement imposed by the prevalence of reduced centers that reside at distances beyond atomic dimensions.

Mechanistic proposals for re-oxidation steps typically invoke bound peroxo (O₂·') intermediates formed via O₂ activation at O-vacancies (**) with concurrent two-electron re-oxidation of the reduced centers [11,20]. Several sequential diffusional hops by one O-atom in the O₂·' intermediates formed can bring O₂·' species near another O-vacency (***) and re-oxidize the reduced center (****) to form another lattice O-atom (O'), thus completing the required four-electron re-oxidation process using O₂ [11,20]. Such steps involve the cleavage and formation of metal-oxygen (M–O) bonds, in processes that have been denoted “inner sphere” O₂ activation routes in homogeneous systems [14,21,22]. Peroxo-type (O₂·') species exhibit detectable UV-visible [23] and Raman [24] features that have been detected during the re-oxidation of reduced CeO₂-based solids by O₂. The detection of bound O₂·' species, however, is infeasible during ODH catalysis, because reduced centers and O₂·'-derived species are present as minority bound species [3,25].

An alternate “outer sphere” O₂ activation mechanism circumvents the need for M–O bond cleavage by effecting re-oxidation through coupled proton-electron-transfer from reduced centers (H/OH•) to O₂(g) to form H₂O₂ [12,14,26,27]. Such routes lead to the appearance of the ¹⁷O-atoms in ¹⁷O₂(g) within H₂O₂ and H₂O molecules, but not in W–O bonds, during the re-oxidation of aqueous W-polyoxometalate anions [14]. The relative contributions of inner and outer O₂ activation routes are quite consequential for alkane ODH selectivity because peroxy (O₂·') intermediates, involved in inner sphere O₂ activation routes, can mediate O-insertion reactions and convert primary alkene products to reactive epoxides that can undergo fast subsequent oxidation to CO and CO₂ [10,11,28,29]. The involvement of O₂·' species in the re-oxidation steps in Mars-van Krevelen ODH cycles and their role in determining product selectivities, however, remain speculative and, for the most part, inaccessible to direct experimental inquiries [10,11].

Here, we provide experimental and theoretical evidence for parallel inner and outer sphere O₂ activation routes during re-oxidation of reduced Mo-based Keggin-type polyoxometalate (POM) clusters and for the presence of O₂·' species. Such species form during the re-oxidation part of Mars-van Krevelen redox cycles and react with alkenes in O-insertion epoxidation reactions. The contributions of these parallel re-oxidation routes are quantitatively assessed by scavenging the O₂·' species with C₃H₈ during alkane ODH catalysis and by density functional theory (DFT) treatments of the relevant intermediates and transition states. Mo-based POM clusters are chosen here as exemplary catalysts because their well-known structure minimizes model uncertainties in benchmarking theory and experiment [3,30], but the methods applied in this work seem general for other reoxy active metal oxides that involve parallel inner and outer sphere O₂ activation routes. CH₃OH and C₂H₅OH dehydrogenation are used as illustrative reactions to form reduced centers, leading to the conclusion that the number, but not the type, of reduced centers depends on the identity and reactivity of the reductants. The analysis and evidence shown here also demonstrate that re-oxidation occurs via inner and outer sphere routes that exhibit much lower activation barriers than conventional mechanisms mediated by diffusional hops of an O-atom in O₂·' intermediates. The combined use of experiment and theory shown in this work provides a method to investigate the kinetic networks for re-oxidation of reduced metal oxides via heterogeneous O₂ activation routes and their connections to homogeneous oxidation catalysis and electro-catalytic and enzymatic systems. These alkanol ODH and alkene epoxidation reactions also uncover a strategy to kinetically couple ODH and epoxidation reactions to form two valuable products, without requiring expensive oxidants such as H₂O₂ molecules that convert to H₂O as a sacrificial reaction [29,31].

2. Methods

2.1. Experimental methods

Supported Mo-based Keggin-type POM clusters (H₃PMo₁₂O₄₀) were prepared by incipient wetness method using SiO₂ (Cab-O-Sil; 304 m² g⁻¹; 1.5 cm³ g⁻¹ pore volume) as a mesoporous support. SiO₂ support was rinsed three times with 1 M HNO₃ (10 cm³ g⁻¹SiO₂) to remove any impurities and then treated in flowing air (UHP Praxair, 0.83 cm³ g⁻¹ s⁻¹) at 383 K for 12 h and at 573 K for 5 h before impregnation with aqueous solutions of H₁PMO₁₂O₄₀ (99.99%, Sigma-Aldrich) to give samples with 25.4% wt. POM, corresponding to a surface density of 0.4 POM nm⁻². Impregnated samples were kept in closed vials at ambient temperature for 24 h and then treated in flowing He (99.999%, Praxair, 0.83 cm³ g⁻¹ s⁻¹) at 323 K for 24 h. The powders were then pressed into pellets, crushed, and sieved to retain 106–180 μm aggregates.
as isolated clusters with two-dimensional structures present only as minority species [3]; their intact Keggin structure was confirmed by $^{31}$P NMR [3].

C$_{6}$H$_{6}$ and CH$_{3}$OH consumption rates and product selectivities were measured on samples (0.05–0.15 g) held within a U-shaped tubular quartz reactor (4 mm inner diameter). The inlet molar rates of O$_{2}$ (99.999% or 25% O$_{2}$/He, Praxair), He (99.999%, Praxair) and H$_{2}$O (doubly-distilled and deionized) were delivered to the reactant streams by syringe pumps (Cole Parmer, 60,061 Series) by vaporizing the liquids at 393 K into the flowing gas stream (O$_{2}$/He or O$_{2}$/He/C$_{3}$H$_{6}$).

Reaction temperatures were maintained using a resistively-heated furnace equipped with an electronic controller (Watlow, Series 988) and were measured with a K-type thermocouple (Omega) placed at a dimple on the outer wall of the quartz reactor. Temperatures of all transfer lines were kept above 393 K in order to prevent condensation of reactants or products. Before contact with reactants, samples were treated in O$_{2}$-H$_{2}$O (20 kPa O$_{2}$ and 2 kPa H$_{2}$O; 0.8 cm$^{3}$ s$^{-1}$) during temperature ramp (0.083 K s$^{-1}$) and for 0.5 h after reaching reaction temperature (453 K). The reactor effluent was analyzed by gas chromatography using a methyl silicone capillary column (HP-1, 25 m × 0.32 mm × 0.5 μm) connected to a flame ionization detector (Agilent 6890 GC) and Poraplot Q and Mol sieve 5A columns connected to a thermal conductivity detector (Agilent 3000A).

Mo-POM (H$_{3}$PMO$_{12}$O$_{40}$) clusters contain protons (H$^+$) that act as Bronsted acids and lattice O-atoms (O$^-$) that act as redox sites. Reactions of alkanols (CH$_{3}$OH or C$_{2}$H$_{5}$OH) and O$_{2}$ mixtures form dehydration products on the acid sites and dehydrogenation products on the redox sites (Scheme S1, Supporting Information) [3]. The POM protons were irreversibly titrated with NH$_{3}$ (1%, Praxair) at 453 K using NH$_{3}$-pulses (4 μmol per pulse; He as a carrier gas, 1.6 cm$^{3}$ s$^{-1}$) during alkanol-O$_{2}$-H$_{2}$O reactions (4 kPa alkanol, 20 kPa O$_{2}$, 2 kPa H$_{2}$O) in order to focus this study on redox properties of Mo-POM, without the molecular complexity and side reactions brought forth by the formation of ethers or alkenes via acid catalysis. NH$_{3}$ pulses were introduced until alkyl dehydration rates became undetectable (< 0.1% of initial rates), indicative of the essential removal of Bronsted acid sites. The changes in dehydration and dehydrogenation rates as a function of NH$_{3}$ doses were shown in Supporting Information (Fig. S1). These NH$_{3}$-titrated samples were used for all alkanol-O$_{2}$ reactions with and without C$_{6}$H$_{6}$ co-reactants after removal of all traces of NH$_{3}$(g) with He (1.6 cm$^{3}$ s$^{-1}$) for 0.2 h. These samples are hereinafter denoted as NH$_{3}$-POM. Dehydration rates on NH$_{3}$-POM remained at nearly undetectable levels throughout all experiments, as expected from the strong binding of NH$_{3}$ at POM protons at 453 K. For comparison, CH$_{3}$OH ODH rates were also measured on H-POM samples with acidic protons.

CH$_{3}$OH, C$_{2}$H$_{5}$OH, and C$_{3}$H$_{6}$ conversions were kept below 3% to maintain constant axial concentrations along the bed and to minimize any effects of the H$_{2}$O formed on rates or selectivities. No conversion of alkanols or C$_{6}$H$_{6}$ was detected on the SiO$_{2}$ support. No detectable amounts of CO and CO$_{2}$ were formed at any of the reaction conditions used. CH$_{3}$OH ODH turnover rates (Γ$_{ODH}$ per POM cluster) are defined as the sum of formaldehyde (HCHO), methylformate (MF) and dimethoxymethane (DMM) molar formation rates (Γ$_{ODH}$ = Γ$_{HCHO}$ + Γ$_{MF}$ + Γ$_{DMM}$), because MF and DMM are formed as secondary products, each from one HCHO molecule (detailed pathways in Scheme S1) [8]. The ODH product selectivity to HCHO on NH$_{3}$-POM remained high (> 60%) at typical reaction conditions (Fig. S2). Acetaldehyde was the only product of C$_{2}$H$_{5}$OH ODH reactions and C$_{3}$H$_{6}$OH ODH rates are reported as acetaldehyde molar formation rates. C$_{6}$H$_{6}$ epoxidation rates (Γ$_{epox}$ per POM cluster) are reported as the sum of the formation rates of propene epoxide (PE) and acetone (Ace) (Γ$_{epox}$ = Γ$_{PE}$ + Γ$_{Ace}$), because acetone is formed only via secondary isomerization of propene oxide [32] in the absence of co-fed H$_{2}$O (residence time studies discussed in Section 3.2).

### 2.2. Computational methods

Plane-wave DFT calculations were performed using Perdew-Wang exchange-correlation functionals (PW91) [33] within the generalized gradient approximation (GGA) as implemented in the Vienna ab initio simulation package (VASP) [34–36]. The valence-core interactions were represented by projector-augmented wave (PAW) methods [37,38], and integer band occupancies were specified in all calculations to properly capture localized-orbital nature of bands for non-periodic system (POM clusters) in periodic plane-wave calculations. An energy cutoff of 400 eV was used to create the plane-wave basis set and a Monkhorst-Pack [39] k-point sampling of $1 \times 1 \times 1$ was used. Electronic structures were minimized self-consistently until the energies between iteration steps differed by less than $1 \times 10^{-6}$ eV and forces on all atoms were less than 0.05 eV Å$^{-1}$.

The structures and energies of Keggin POM clusters, bound intermediates and transition states on POM clusters, and gaseous molecules were calculated by placing them at the center of $2 \times 2 \times 2$ nm cubic cell in order to avoid interactions among adsorbates or transition states in adjacent cells; larger cubic cells ($3 \times 3 \times 3$ nm) gave the same value for CH$_{3}$OH adsorption energies on O$^-$ sites. The central P atom in each POM cluster was fixed to prevent net translation of the cluster, but all other atoms were relaxed during geometry and energy optimizations. Long-range interactions among atoms located in neighboring unit cells were corrected using dipole and quadrupole moments calculated by taking the center of the unit cell as the center of charge distributions [40].

The lowest energy electronic structures for each reaction intermediate were determined by comparing energies obtained with singlet (spin-restricted and spin-polarized) and triplet spin multiplicities. The minimum energy paths (MEPs) connecting reaction intermediates were obtained using nudged elastic band (NEB) methods [41] with structures converged to energies within $1 \times 10^{-6}$ eV and forces within 0.1 eV Å$^{-1}$. The NEB calculations were performed on both singlet and triplet potential energy surfaces to identify crossing points of the MEP connecting intermediates of different multiplicities. The structures near the maximum of an MEP or at the crossing points were used to locate the transition states using the Henkelman’s Dimer method [42] with the convergence criteria of $< 1 \times 10^{-7}$ eV for energies and $< 0.05$ eV Å$^{-1}$ for forces on atoms. Transition state searches near the spin-crossing points were performed in an open-shell singlet state using Dimer calculations, and their energies were compared to those for the singlet (closed-shell) and triplet states.

Vibrational frequencies were calculated by diagonalizing the Hessian matrix of second derivatives of the energy with respect to atomic positions in order to estimate their contribution to thermodynamic properties of intermediates and transition states. Enthalpies and free energies include contributions from electronic energies ($E_0$), zero-point vibrational energies (ZPVE) and finite temperature contributions from vibrations and, for gaseous species, translations and rotations:

$$H = E_0 + ZPVE + H_{ vib} + H_{ trans} + H_{ rot}$$ (1)

$$G = E_0 + ZPVE + G_{ vib} + G_{ trans} + G_{ rot}$$ (2)
Low-frequency modes (less than ~150 cm\(^{-1}\)) of weakly bound adsorbates and transition states lead to significant errors in entropies and free energies, and therefore, their contributions are instead substituted by a fraction (0.7) of the translational and rotational entropies of relevant gas phase molecules [43], unless otherwise stated.

DFT-derived free energies are used to estimate kinetic constants for elementary steps using the formalism of transition state theory;

\[
k = \frac{k_B T}{h} \exp \left( -\frac{\Delta G^1}{RT} \right)
\]

where \(\Delta G^1\) represents the difference in free energies between the transition state (TS) and its relevant precursor. \(k_B\) is Boltzmann’s constant, \(h\) is Planck’s constant, and \(R\) is the gas constant. Thermodynamic constants of equilibrated steps are related to their standard free energy changes for the reaction (\(\Delta G^2\));

\[
K = \exp \left( -\frac{\Delta G^2}{RT} \right)
\]

3. Results and discussion

3.1. CH\(_3\)OH-O\(_2\) reactions on H-POM and NH\(_4\)-POM

CH\(_3\)OH ODH rates increased linearly with CH\(_3\)OH pressure (<1 kPa CH\(_3\)OH) on both H-POM and NH\(_4\)-POM (i.e., before and after titration of protons by NH\(_3\), but became less sensitive to CH\(_3\)OH pressure with increasing pressure (0.1–4 kPa; 453 K; Fig. 1a). ODH rates were independent of O\(_2\) pressure at all O\(_2\) pressures (1–35 kPa; 453 K; Fig. 1b). These trends are consistent with those in previous studies [3,9] and with H-abstraction from adsorbed CH\(_3\)OH by lattice O-atoms (O\(^*\)) as the sole kinetically-relevant step in ODH turnovers (step 2; Scheme 2); such turnovers are completed by fast re-oxidation steps.

This mechanistic proposal is consistent with the rate equation [3];

\[
r_{\text{ODH}} = \frac{k_{\text{ODH}} P_{\text{CH}_3\text{OH}}}{1 + K_{\text{CH}_3\text{OH}} P_{\text{CH}_3\text{OH}}}
\]

Here, \(K_{\text{CH}_3\text{OH}}\) denotes the equilibrium constant for molecular adsorption of CH\(_3\)OH onto O\(^*\) (step 1a; Scheme 2) and depends on the free energy of CH\(_3\)OH adsorbed on O\(^*\) (CH\(_3\)OH-O\(^*\)) with respect to its CH\(_3\)OH(g) and O\(^*\) precursors. The \(k_{\text{ODH}} = k_{\text{ODH}} K_{\text{CH}_3\text{OH}}\)

![Fig. 1](image_url)

**Fig. 1.** CH\(_3\)OH ODH rates (per POM-ks) measured from CH\(_3\)OH-O\(_2\) mixtures on H-POM (A) and NH\(_4\)-POM (O) at 453 K as a function of (a) CH\(_3\)OH pressure (0.1–4 kPa) at 20 kPa O\(_2\) and (b) O\(_2\) pressure (1–35 kPa) at 4 kPa CH\(_3\)OH. Dashed curves represent the best regression fits to the functional form of Eq. (5).
term is the first-order rate constant for CH₃OH ODH on O* and reflects the free energy of a kinetically-relevant H-abstraction TS (step 2; Scheme 2) with respect to its CH₂OH(g) and O* precursors. The two denominator terms reflect the relative coverages of O* and CH₂OH-O*. ODH rates become zero-order in CH₂OH at high CH₂OH pressures, indicative of a shift from O* to CH₂OH-O* as the most abundant surface intermediate (MASI) with increasing CH₂OH pressure. The functional form of Eq. (5) accurately describes measured CH₂OH ODH rates (Fig. 1) and the regression of these data to the functional form of Eq. (5) gives the $k_{\text{ODH}}$ and $k_{\text{Apzym}}$ values on these catalysts (Table S1, SI).

Measured $k_{\text{ODH}}$ values were ten-fold smaller on NH₄-POM (0.5 ± 0.1 (kPa POM ks)⁻¹) than on H-POM (5 ± 1 (kPa POM ks)⁻¹), as a result of a decrease in the H-atom abstraction ability of lattice O-atoms (O*) when the replacement of H⁺ with NH₄⁺ leads to a higher electron density in the oxide clusters [3]. Such H-atom abstraction ability of O* is determined by the stability of O–H bonds that are nearly formed at the H-abstraction TS [3,9]; the strength of these O–H bonds is given by DFT-derived H-atom addition energy (HAE) (detailed calculation methods described in SI, Section S2) [3]. Reactivity-averaged HAE values (HAE) [3] over all accessible O-atoms in POM clusters become less negative upon titration of protons by NH₃ (+ 303 to –292 kJ mol⁻¹ on H-POM and –303 to –292 kJ mol⁻¹ on NH₄-POM; Table S1, SI), consistent with O-atoms that are weaker H-abstractors in NH₄-POM than in H-POM clusters and with the lower ODH turnover rates observed on NH₄-POM clusters.

DFT treatments of intermediates and transition states in the reduction (Scheme 2) and re-oxidation (Scheme 3) sequences of elementary steps were carried out at a specific location within the POM clusters, consisting of a vicinal bridging O-atoms pair (O₁ and O₂; atom locations indicated in Fig. 2) that exhibits one of the most negative HAE values. Such values make this pair a likely location for ODH turnovers [3]. The shift in (HAE) toward less negative values upon replacement of H⁺ with NH₄⁺ (–303 to –292 kJ mol⁻¹) leads to increase in DFT-derived free energy barriers for the kinetically-relevant H-abstraction step (step 2; Scheme 2) from 111 to 139 kJ mol⁻¹ (453 K, 1 bar CH₃OH; Table S1). Measured $k_{\text{Apzym}}$ values were similar on H and NH₄ forms of POM clusters (0.8 ± 0.3 kPa⁻¹ and 0.4 ± 0.1 for H-POM and NH₄-POM, respectively; Table S1). Their similar and near unity values are consistent with DFT-derived CH₃OH adsorption free energies, which were –1 and –2 kJ mol⁻¹ on O₂ in H-POM and NH₄-POM, respectively (453 K, 1 bar CH₃OH; Table S1).

ODH rates were not affected by O₂ pressure (Fig. 1b), reflecting the prevalence of O* species and presence of reduced centers and O₂-derived intermediates as minority species. Such kinetic trends are consistent with facile re-oxidation events but do not provide any insights into the nature or rates of the O₂ activation pathways. Consequently, inferences about the mechanism and the identity and reactive properties of O₂-derived intermediates require their reactive scavenging to form specific products during ODH reactivity-averaged HAE values on NH₄-POM clusters by O₂(g) and the decomposition of bound peroxy (OO*) species and gaseous H₂O₂ molecules. Quasi-equilibrated steps are denoted by oval symbols superimposed over double arrows. Nomenclatures for reactive species are shown in parentheses under each structure. Recombinative desorption of H₂O from H/OH* generates * or H/OH*) to regenerate O* and release H₂O, or with O* to form OO* and H₂O (steps 6a and 6b).

### 3.2. CH₃OH-O₂-C₃H₆ reactions on NH₄-POM clusters

The use of NH₄-POM clusters (instead of H-POM) prevents alkene oligomerization and alkane elimination and condensation reactions that occur readily on Brønsted acids; these side reactions form oligomers that block active sites of protons (H⁺) and lattice O-atoms (O*) in H-POM clusters, especially when CH₃OH is added to CH₂OH-O₂ reactants (Fig. S3). In contrast with CH₃OH-O₂-C₃H₆ reactions on H-POM clusters, CH₂OH ODH and CH₃H₆ epoxidation on NH₄-POM did not show detectable deactivation (Fig. S4). The titration of protons by NH₃ also inhibited CH₃H₆ hydration to 2-propanol, which can subsequently dehydrogenate on O* sites to form acetone, a molecule that can also be formed via hydride shifts in propene oxide, the primary product in propene epoxidation.

CH₃H₆ epoxidation products were detected on NH₄-POM only when CH₂OH was also present in O₂-C₃H₆ mixtures at 453 K, indicating that lattice O-atoms (O*) in NH₄-POM clusters on their own cannot catalyze epoxidation turnovers. Epoxidation events require that CH₂OH molecules dehydrogenate at O* sites and form reduced centers, which can then react with O₂ to form the electrophilic dioxygen species that are required for inserting an O-atom into the C=C bonds of C₃H₆. Such O₂ activation routes have been
proposed to involve bound peroxo (OO\(^*\)) species \[11,20,29\] and are denoted as “inner sphere O\(_2\) activation routes” \[14,21\], because they require the formation of metal-oxygen (M–O) bonds via OO\(^*\) intermediates.

The primary epoxidation product, propene epoxide, subsequently isomerizes to acetone \[32\], leading toacetone to propene epoxide molar ratios that increase linearly with increasing C\(_3\)H\(_6\) conversion but extrapolate to zero values as conversion decreases (Fig. S5). Epoxidation rates \(r_{\text{Epox}}\) are thus given by the combined molar formation rates of propene epoxide \(r_{\text{PE}}\) and acetone \(r_{\text{Ace}}\).

The effects of C\(_3\)H\(_6\), H\(_2\)O, CH\(_3\)OH, and O\(_2\) pressures on CH\(_3\)OH ODH and C\(_3\)H\(_6\) epoxidation rates are examined next in the context of plausible O\(_2\) activation elementary steps.

### 3.2.1. Effect of C\(_3\)H\(_6\) on CH\(_3\)OH ODH and C\(_3\)H\(_6\) epoxidation rates

CH\(_3\)OH ODH rates were essentially unaffected by changes in C\(_3\)H\(_6\) pressure (0–35 kPa; 453 K; Fig. 3a), indicating that C\(_3\)H\(_6\)-derived bound species are present at low coverages on O\(^*\) (step 1c; Scheme 2). Thus, C\(_3\)H\(_6\)-epoxidation rates can be used to identify the involvement of bound O\(_2\)-derived intermediates during re-oxidation events and their reactivity for O-insertion reactions, without disturbing the ODH pathways that form reduced centers.

Epoxidation rates were much lower than ODH rates at low C\(_3\)H\(_6\) pressures, but increased with increasing C\(_3\)H\(_6\) pressure and approached a constant value above 8 kPa C\(_3\)H\(_6\) (Fig. 3a); this constant value corresponds to maximum epoxidation rates that are about ten-fold smaller than ODH reaction rates.

Schemes 2 and 3 show plausible routes for the reduction \[3,44\] and re-oxidation \[11,14,21,44\] of NH\(_4\)-POM clusters during CH\(_3\)OH ODH occurring via Mars-van Krevelen redox cycles. Re-oxidation routes also include a step accounting for the scavenging of bound O\(_2\)-derived species via C\(_3\)H\(_6\) epoxidation \[29,45\]. In the NH\(_4\)-POM reduction steps, the molecular adsorption of CH\(_3\)OH on lattice O-atoms (O\(^*\); step 1a; Scheme 2) precedes the kinetically-relevant H-abstraction step to form HCHO and a vicinal hydroxyl pair (H/ OH\(^*\); step 2; Scheme 2) \[3,44\]. H\(_2\)O and C\(_3\)H\(_6\) molecules can also adsorb and occupy active O\(^*\) species (steps 1b and 1c; Scheme 2), thus possibly inhibiting ODH rates.

Reduced centers consisting of H/OH\(^*\) formed via step 2 in Scheme 2 must be re-oxidized by O\(_2\) to regenerate the oxidized centers (O\(^*\)), required for subsequent ODH turnovers. The discussion that follows provides a formalism to probe two specific branching points along the re-oxidation sequences shown in Scheme 3. At one juncture, O\(_2\) activation occurs via either inner and outer sphere routes to form O\(_2\)-derived species with concurrent two-electron re-oxidization of reduced NH\(_4\)-POM clusters (steps 4a and 4b; Scheme 3). At the other branching point, OO\(^*\) consumption can occur via parallel reactions with either CH\(_3\)OH or C\(_3\)H\(_6\) (steps 5a and 5b; Scheme 3). The kinetic responses of epoxidation and ODH rates and their ratios to C\(_3\)H\(_6\) pressure are discussed in the context of the contributions of the parallel routes at these two branching points.

Inner sphere routes involve recombinative H\(_2\)O desorption from H/OH\(^*\) to form O-vacancies (\(^*\)) (step 3; Scheme 3). Subsequent O\(_2\)
activation at * forms bound peroxy (OO’) species (step 4a; Scheme 3), which can be scavenged by C3H6 to form epoxide with the regeneration of one O’ (step 5b; Scheme 3). The rate of epoxidation (rEpox) via OO’ species is given by:

\[ r_{\text{Epox}} = k_{\text{Epox}} P_{\text{C3H6}}[\text{OO’}] , \]

where \( k_{\text{Epox}} \) denotes the first-order rate constant for C3H6 epoxidation on OO’ (step 5b; Scheme 3) and depends on the free energy difference between a kinetically-relevant O-insertion TS and its C3H6(g) and OO’ precursors. When C3H6 epoxidation accounts for all OO’ consumption events, the pseudo-steady-state concentration of OO’ species is given by the ratio of their formation rate (\( r_{\text{OO’}} \)) to \( k_{\text{Epox}} P_{\text{C3H6}} \):

\[ [\text{OO’}] = \frac{r_{\text{OO’}}}{k_{\text{Epox}} P_{\text{C3H6}}} . \]

which upon substitution into Eq. (6) would lead to \( r_{\text{Epox}} \) values that are independent of C3H6 pressure and equal to \( r_{\text{OO’}} \) at all pressures. Measured epoxidation rates, however, initially increased with increasing C3H6 pressure before reaching a constant value (Fig. 3a). These trends are indicative of the involvement of alternate OO’ consumption routes that compete with epoxidation events and which must occur in order to complete the re-oxidation pathways in the absence of C3H6. DFT calculations suggest that such routes may involve OO’ decomposition via reactions with CH3OH (step 5a; Scheme 3), ultimately leading to the regeneration of O’ along with a formation of HCHO and H2O (Section 3.5.1).

The initial increase in epoxidation rates with C3H6 pressure (<8 kPa; Fig. 3a) is consistent with larger contributions from epoxidation routes (step 5b; Scheme 3) than from alternate routes (step 5a; Scheme 3) to OO’ consumption rates as the C3H6 to CH3OH pressure ratio increases. The epoxidation rates become less sensitive to C3H6 pressure (>8 kPa) as most of the OO’ species are scavenged by C3H6 instead of CH3OH and reach asymptotic values that reflect epoxidation rates that become equal to those for OO’ formation (\( r_{\text{OO’}} \), Eqs. (6) and (7)). The ratios of NH4-POM reduction by CH3OH dehydrogenation (step 2; Scheme 2) must be equal to the re-oxidation rates at steady-state; therefore, these asymptotic values would equal the CH3OH ODH rates when all reduced centers formed via ODH steps are re-oxidized via the formation of OO’ intermediates. Asymptotic epoxidation rates, however, are much lower than the other rates (Fig. 3a), indicative of the involvement of alternate re-oxidation routes that exclude OO’ intermediates.

Such conclusions are also evident from the ratios of the rates of epoxidation and ODH (\( r_{\text{Epox}}/r_{\text{ODH}} \), shown as a function of C3H6 pressure (0–35 kPa; 453 K) in Fig. 4. The asymptotic (\( r_{\text{Epox}}/r_{\text{ODH}} \)) ratios (for C3H6/CH3OH > 8) reflect conditions for which OO’ consumption via epoxidation routes is dominant (i.e., without contributions from step 5a in Scheme 3); therefore, ODH rates exclusively reflect the reduction rates of NH4-POM clusters that must equal their re-oxidation rates at steady-state. Thus, asymptotic \( r_{\text{Epox}}/r_{\text{ODH}} \) values represent the fraction of re-oxidation events that occur through OO’ intermediates. These fractions are much smaller than unity (<0.1; Fig. 4), consistent with the prevalent involvement of re-oxidation pathways other than OO’-mediated routes to re-oxidation rates.

These alternate re-oxidation routes may involve proton-coupled electron-transfer from vicinal OH pairs (H/\( \text{OH}^+ \)) at reduced centers to gaseous or weakly-bound O2 leading to the formation of H2O2 (step 4b; Scheme 3). These processes are known to occur in liquid media and are denoted as “outer sphere” routes, because they do not disturb the inner coordination sphere of the metal centers or the covalent M–O bonds [12,14]. The H2O2 formed in these two-electron re-oxidation steps can diffuse and re-oxidize another two-electron reduced center (* or H/\( \text{OH}^+ \); step 6a; Scheme 3) [12], thus completing the four-electron re-oxidation process required for O2(g) to act as the stoichiometric oxidant in Mars-van Krevelen cycles. The involvement of parallel inner and outer sphere O2 activation routes (steps 4a and 4b; Scheme 3) is consistent with DFT-derived activation free energies, as shown by detailed assessments of energies for intermediates and transition states involved in these two O2 activation pathways (Section 3.3).

3.2.2. Effects of H2O on CH3OH ODH and C3H6 epoxidation rates

The re-oxidation steps in Scheme 3 include parallel inner and outer sphere O2 activation routes mediated by O2 reactions with either * or \( \text{H/} \text{OH}^+ \) to form OO’ or H2O2, respectively (steps 4a and 4b; Scheme 3). As a result, their relative contributions depend on the ratio of * and \( \text{H/} \text{OH}^+ \) coverages ([*]/[\( \text{H/} \text{OH}^+ \)]), which decreases with increasing H2O pressure as a consequence of the equilibration of step 3 (Scheme 3). These effects of H2O are probed here by measuring \( r_{\text{Epox}}/r_{\text{ODH}} \) ratios at different H2O pressures and high C3H6/CH3OH ratios to ensure that OO’ species exclusively react with C3H6 to form epoxidation products (step 5b; Scheme 3) instead of reacting with CH3OH (step 5a; Scheme 3).

CH3OH ODH rates (without added C3H6) decreased with increasing H2O pressure (Fig. S6) because of competitive adsorption of H2O with CH3OH on O’ (steps 1a and 1b; Scheme 2) [3];

\[ r_{\text{ODH}} = \frac{k'_{\text{ODH}} P_{\text{CH3OH}}}{1 + K_{\text{CH3OH}} P_{\text{CH3OH}} + K_{\text{H2O}} P_{\text{H2O}}} . \]

Here, \( K_{\text{CH3OH}} \) and \( K_{\text{H2O}} \) are the equilibrium constants for molecular adsorption of CH3OH and H2O on O’, respectively (steps 1a and 1b; Scheme 2), and \( k'_{\text{ODH}} = K_{\text{CH3OH}} k_{\text{ODH}} \) denotes the first-order rate constant for CH3OH ODH (step 2; Scheme 2). The functional form of Eq. (8) accurately describes all rate data (Fig. S6) with larger re-oxidation values for \( r_{\text{ODH}} \) (8 ± 4 kPa–1) than for \( K_{\text{CH3OH}} \) (0.4 ± 0.1 kPa–1).

CH3OH ODH and C3H6 epoxidation rates are shown in Fig. 3b as a function of H2O pressure (0.01–45 kPa; 453 K). Acetone can be formed via propene oxide isomerization but also via C3H6 hydration when H2O is co-fed; such contributions were excluded from
C$_3$H$_6$ conversion rates by subtracting acetonitrile formation rates measured with O$_2$-C$_2$H$_5$OH mixtures from those measured with CH$_3$OH-O$_2$-C$_2$H$_5$OH reactants (details in SI, Section S4). ODH rates decreased with increasing H$_2$O pressure, but epoxidation rates decreased even more strongly (Fig. 3b), as evident from $r_{PO}/r_{ODH}$ ratios that decreased with increasing H$_2$O pressure (Fig. 4). These $r_{PO}/r_{ODH}$ ratios reflect the fraction of re-oxidation events occurring via OO*-mediated inner sphere routes. Consequently, these data are consistent with a shift from * to H/OH* via the equilibration of step 3 (Scheme 3) and with a concomitant preference for outer sphere routes as H$_2$O concentrations increase (step 4b; Scheme 3).

The formation of C$_3$H$_6$ epoxidation products from CH$_3$OH-O$_2$-C$_2$H$_5$OH reactions, but not from O$_2$-C$_2$H$_5$OH reactions, indicates that inner sphere routes mediated by bound peroxo (OO*) species are involved in the re-oxidation of reduced NH$_4$-POM by O$_2$, as also proposed in O$_2$ activation during homogeneous oxidations [12–14], because such O$_2$-derived species are active for insertion of O-atoms into alkenes [46,47]. These reaction routes are also found in monoxygenase enzymes that form electrophilic peroxo (OO*) species via O$_2$ reactions with two-electron reduced centers to perform O-insertions into C=C or C=H bonds in alkenes, alkenes and arenes [15]. These mechanisms, demonstrated here for oxidation of gaseous substrates on solid catalysts, offer strategies for using alkanes as sacrificial reductants to form bound peroxo (OO*) species for propene epoxidation, while forming alkanes as useful co-products. Therefore, these epoxidation routes using sacrificial reductants, after appropriate optimization, may provide alternatives to H$_2$O$_2$ and organic peroxides as epoxidation reagents, an approach considered in homogeneous systems [46,47].

OO*-mediated inner sphere routes, however, account for only a fraction of the re-oxidation events (<0.1; Fig. 4). Their contributions become even smaller when H$_2$O was added (Fig. 4) because the conversion of reduced centers from * to H/OH* (step 3; Scheme 3) favors outer sphere routes (step 4b; Scheme 3). The mechanistic features and redox properties that control the relative rates of inner and outer sphere re-oxidation routes are thus essential to choose catalysts and conditions that favor the inner sphere routes that lead to epoxidation turnovers. Such inquiries of providing details of elementary steps and the quantitative assessment of the two O$_2$ activation routes during ODH turnovers are achieved using DFT calculations on relevant intermediates and transition states involved in re-oxidation steps, which are discussed next.

3.3. Density functional theory assessment of intermediates and rates for inner and outer sphere O$_2$ activation routes

Inner sphere O$_2$ activation routes involve quasi-equilibrated recombinative desorption of H$_2$O from vicinal OH groups (H/OH*) to form O-vacancies (*) and the subsequent irreversible O$_2$ activation on * to form OO* (steps 3 and 4a; Scheme 3). Their rate ($r_{in}$) is given by:

$$r_{in} = k_{in} P_{O_2} [\ast] = \frac{k_{in}}{K_w} P_{O_2} [H/OH^*] = \frac{k_{in}}{k_{out}} P_{O_2} [H/OH^*]$$

(9)

$K_w$ denotes the equilibrium constant for the interconversion of H/OH* to form * (step 3; Scheme 3) and $k_{in}$ denotes the first-order rate constant for O$_2$ activation on * to form OO* (step 4a; Scheme 3). The rate of outer sphere routes ($r_{out}$) to form H$_2$O$_2$(g) via irreversible O$_2$ activation on H/OH* species (steps 4b; Scheme 3) is given by:

$$r_{out} = k_{out} P_{O_2} [H/OH^*]$$

(10)

where $k_{out}$ denotes the first-order rate constant for O$_2$ activation on H/OH* to form H$_2$O$_2$(g) (step 4b; Scheme 3).

Efficient epoxidation events during CH$_3$OH ODH turnovers require the catalytic system to preferentially re-oxidize via OO*-mediated inner sphere routes. The contributions from inner and outer sphere O$_2$ activation are given by their rate ratios ($r_{in}/r_{out}$ defined as $\chi$):

$$\chi = \frac{r_{in}}{r_{out}} = \frac{k_{in} P_{O_2} [\ast]}{k_{out} P_{O_2} [H/OH^*]} = \frac{k_{in}}{k_{out}}$$

(11)

which depends on the ratio of the respective rate parameters ($k_{in}/k_{out}$) and on the H$_2$O pressure. These rate parameters, $k_{in}$ ($=k_{in}/k_{out}$) and $k_{out}$, reflect in turn the free energies of formation of the transition states for inner and outer sphere O$_2$ activation routes from common O$_2$(g) and H/OH* precursors; their values are examined next using DFT methods.

3.3.1. Mechanistic details of inner and outer sphere O$_2$ activation routes

Gaseous O$_2$ in its most stable triplet ground state (two unpaired p-electrons) reacts with reduced centers (* or H/OH*) to form O$_2$-derived species (OO* or H$_2$O$_2$) that are more stable in their singlet states (no unpaired electrons) [11]. Consequently, their respective singlet and triplet potential energy surfaces (PES) must cross along their interconversion reaction coordinate, potentially leading to broken-symmetry singlet states at the crossing point; these electronic structures can have lower energies than singlet or triplet states because of spin-orbit coupling [10]. The spin-crossings are examined here by calculating minimum energy paths (MEPs) for both singlet and triplet states using nudge elastic band (NEB) methods [41]; the existence of broken-symmetry transition states near the crossing-points is examined by performing spin-unrestricted Dimer calculations [42] with singlet multiplicity. The evidence for symmetry-breaking in converged transition states becomes apparent from the existence of non-degenerate energy levels for electrons of opposite spins, in spite of their singlet states, and from their lower energies compared to those derived from spin-restricted-singlet and triplet calculations.

The spin crossing for inner sphere O$_2$ activation routes on NH$_4$-POM clusters (step 4a; Scheme 3) is shown in Fig. 5. Fig. 5a shows a MEP connecting a triplet O$_2$(g) to a triplet OO* species, together with singlet state (spin-polarized) unrelaxed single-point energies of all structures in this MEP. Fig. 5b shows a MEP for singlet states (spin-polarized) together with corresponding triplet single-point energies. Both versions of these calculations (Fig. 5a and 5b) show that the reactant O$_2$(g) is more stable in its triplet state, while the bound peroxo (OO*) product is more stable in the singlet state. The initial O$_2$ adsorption goes through a local maximum energy on the triplet path before a spin-crossing that occurs at a lower energy than this maximum and leads to a singlet OO* species with even lower energy. Taken together, these trends show that the maximum in the combined MEP occurs on the triplet PES, instead of the singlet-triplet crossing point. This maximum corresponds to a triplet TS obtained using Dimer method [42] (denoted TS$_{in}$, Fig. 5), which has an electronic energy of 141 kJ mol$^{-1}$ before ZPVE corrections relative to O$_2$(g) and H/OH* precursors.

O$_2$ reactions with transition-metals can lead to peroxo species (OO*) through either concerted [22,48] or sequential [49,50] transfer of two electrons to dioxygen. In the stepwise mechanism, the first electron transfer to O$_2$ forms σ-superoxo intermediates, which convert to σ$^*$-superoxo species via subsequent electron-transfer, at which point the triplet-to-singlet crossing occurs [49,50]. Such mechanism was previously suggested for O$_2$ activation on transition-metal complexes of Pd [49], Co [50], Ir [50], and Ru [50]. An analogous stepwise mechanism is suggested by the MEP for inner sphere O$_2$ activation routes on NH$_4$-POM clusters (Fig. 5) with TS$_{in}$ representing that for the first electron-transfer...
step to form $\eta^1$-superoxo. The $O_2$ moiety in TS$_{\text{in}}$ (Fig. 6f) assumes an end-on ($g_1$) geometry with an $O-O$ bond distance of 0.125 nm, which lies between the bond distances in $O_2(g)$ (0.123 nm) and in $g_1$-superoxo complexes of transition metals (0.128–0.130 nm) [51,52]. The $O_2$ moiety at TS$_{\text{in}}$ also acquires a negative charge that is much smaller than for a full electron (−0.12 e$^-$/C$_0$). The under-coordinated O-atom in TS$_{\text{in}}$ (O−-atom; Fig. 6f) reacts with the Mo center and converts to the $g_2$-peroxo products (Fig. 6g) via a kinetically-irrelevant second electron-transfer step; no other barrier was found between TS$_{\text{in}}$ and $g_2$-superoxo product (Fig. 5).

The bound peroxo (OO$^*$) product state on NH$_4$-POM clusters has an $O=O$ bond length (0.143 nm;Fig. 6g) similar to that for side-on $g_2$-peroxo-Mo complexes (0.148 nm) [52] and a negative charge slightly greater than a full electron ($-1.1$ e$^-$/C$_0$) at the $O_2$ moiety.

The MEP for outer sphere $O_2$ activation routes, involving $H_2O_2$ formation via $O_2$ reactions with $H/OH^*$ (step 4b; Scheme 3), includes a sequential transfer of two H-atoms in $H/OH^*$ to $O_2(g)$. They are shown in Fig. 5c and 5d for the triplet and singlet (spin-polarized) NEB calculations, respectively. The first H-atom transfer to $O_2(g)$ forms a bound OOH intermediate in the triplet state via a TS (TS$_{\text{out}}$ (a)) also in the triplet state (Fig. 5c). The OOH intermediate exhibits a radical-like character (OOH), evidenced by its energy more stable in triplet state than in singlet state, because charged HOO- species would exist in its singlet form. Its radical nature is also evident from spin density maps that indicate the presence of unpaired electrons in OOH (Fig. S9). The singlet and triplet MEP curves cross as the second H-atom is transferred, leading to $H_2O_2$ products in their stable singlet state. A dimer calculation starting with the structure at the crossing point gave a broken-symmetry TS (TS$_{\text{out}}$ (b); Fig. 5d), as evident from its energy lower than both spin-restricted singlet and triplet states [10]. The TS for the first H-atom transfer (TS$_{\text{out}}$ (a); Fig. 6i) lies at the highest energy point along the MEP with a 14 kJ mol$^{-1}$ barrier (electronic energy without ZPVE corrections) relative to $O_2(g)$ and $H/OH^*$ precursors. The TS for the second H-atom transfer (TS$_{\text{out}}$ (b); Fig. S10) exhibits a slightly lower barrier (9 kJ mol$^{-1}$, electronic energy without ZPVE corrections), indicating that the second H-atom transfer step is faster and thus kinetically-irrelevant. DFT-derived MEP curves show that two-electron $O_2$ activation routes on NH$_4$-POM clusters involve a stepwise mechanism for both inner and outer sphere routes, with the first step exhibiting the higher barrier and limiting the reactions.

### 3.3.2. Gibbs free energies of intermediates and transition states involved in $O_2$ activation via inner and outer sphere routes

A more rigorous assessment of the relative contributions of these two $O_2$ activation routes requires accurate estimates of Gibbs free energies, which are discussed next for all intermediates and transition states involved in inner and outer sphere $O_2$ activation routes (steps 3, 4a and 4b; Scheme 3). Free energies are calculated at 453 K and 1 bar of gaseous species for both routes.

**Inner sphere routes** require the recombination of two hydroxyl groups in $H/OH^*$ (Fig. 6a) to form $H_2O^*$ (Fig. 6c). This step is endergonic with a free energy change of 59 kJ mol$^{-1}$ and involves a TS...
(TS_{sw}, Fig. 6b) with a free energy barrier of 70 kJ mol\(^{-1}\). The subsequent desorption of H\(_2\)O forms an O-vacancy (*; Fig. 6d), which is slightly endoergic (\(\Delta G_{\text{des}} = 5\) kJ mol\(^{-1}\)) in spite of the entropy gained upon H\(_2\)O desorption, indicative of the enthalpic instability of O-vacancies (electronic energies, entropies, enthalpies, and free energies for all species; Table S2; SI). Molecular adsorption of O\(_2\) on O-vacancies (*) is also endoergic (\(\Delta G_{\text{ads}} = 21\) kJ mol\(^{-1}\)) because of weak binding and of the loss of translational entropy upon O\(_2\) binding. Bound O\(_2\) species at * (\(-\text{O}_2\); Fig. 6e) react via a TS (TS_{in}; Fig. 6f) and this step has a free energy barrier of 22 kJ mol\(^{-1}\) (referenced to bound O\(_2\) and *) to form OO* species (Fig. 6g). This O\(_2\) activation step imposes the highest barrier (step 4a; Scheme 3) along the inner sphere reaction coordinate, suggesting that the formation of * and H\(_2\)O(g) from H/OH* is quasi-equilibrated (step 3; Scheme 3). Such equilibration is consistent with the decrease in \(r_{\text{Epox}}/r_{\text{ODH}}\) ratios upon adding H\(_2\)O due to a shift in the * and H/OH* equilibrium towards the latter (Fig. 4).

In the outer sphere routes (step 4b; Scheme 3), O\(_2\)(g) adsorbs weakly on H/OH* (\(\Delta G_{\text{ads}} = 22\) kJ mol\(^{-1}\); H/OH*-O\(_2\), Fig. 6h). Bound O\(_2\) species react with surface O-H bonds to form H\(_2\)O\(_2\) and O* (O*-H\(_2\)O\(_2\); Fig. 6j) via a TS (TS_{out}; Fig. 6i), and this O\(_2\) activation step has a free energy barrier of 56 kJ mol\(^{-1}\), referenced to bound O\(_2\) and H/OH*. H\(_2\)O\(_2\) molecules bound on O* desorb in an exoergic step (\(\Delta G_{\text{des}} = -10\) kJ mol\(^{-1}\)).

The kinetic relevance of inner and outer sphere O\(_2\) activation routes during re-oxidation events can be assessed by their rate ratios (\(r_{\text{in}}/r_{\text{out}}\), defined as \(\chi\); Eq. (11)), which depends on the ratio of the respective rate parameters (\(k_{\text{in}}/k_{\text{out}}\)) and on the H\(_2\)O pressure. These rate parameters, \(k_{\text{in}}\) (\(k_{\text{in}}/k_{\text{out}}\)) and \(k_{\text{out}}\), reflect the free energies of O\(_2\) activation transition states that are referenced to the common precursors of O\(_2\)(g) and H/OH*, as shown in Fig. 6 (107 and 78 kJ mol\(^{-1}\) for TS_{in} and TS_{out}, respectively). The values of \(\chi\), calculated using these DFT-derived free energies, and their comparisons to experimental values are discussed next.
3.3.3. DFT-derived assessment of the relative contributions of inner and outer sphere O₂ activation routes

DFT-derived electronic energies, enthalpies, entropies and free energies for O₂ activation via inner and outer sphere routes are shown in Table 1. Uncertainties in calculating low-frequency vibrational modes (less than ~150 cm⁻¹) of weakly bound adsorbates and transition states can lead to significant errors in thermodynamic properties. Therefore, zero-point energies, enthalpy and entropy values are obtained by substituting the contributions of low-frequency modes with 0.7 times the translational and rotational modes of O₂(g), inspired by the experimental data suggesting that weakly adsorbed molecules on oxide surfaces retain 0.7 of entropy of corresponding gaseous molecules [43]. At the limit where O₂ moiety in transition states does not retain any translational and rotational degree of freedom, these low-frequency modes can be fully removed from vibrational partition functions, and thermodynamic properties calculated using such treatments can lead to significant errors in thermodynamic properties. Therefore, zero-point energies, enthalpy and entropy values are obtained by substituting the contributions of low-frequency vibrations with 0.7 of their substitution by translations and rotations (the solid line; Fig. 7a), suggesting that the transition state for the inner sphere route has greater entropy contributions from weak surface modes. The slopes of trends with temperature (Fig. 7a), however, were similar for both types of calculations, consistent with small effects of such treatments on enthalpies. The experimental rate ratio (χ = rin/rout) is obtained by regressing the rate data in Figs. 3 and 9 to the functional form of the rate equations for ODH and epoxidation (rate equations and estimated parameters in Scheme 4), derived from the elementary steps in Schemes 2 and 3 (derivation in Section S10, SI). Its value (0.1 at 0.01 kPa H₂O, 453 K) lies within the two sets of DFT-derived values for the two different assumptions about low-frequency vibrational modes (0.01 < χ < 4.4; 0.01 kPa H₂O; 453 K; Fig. 7a).

The χ values increase with increasing temperature (Fig. 7b), indicating that inner sphere routes become more prevalent at higher temperatures, consistent with the higher activation enthalpies for the inner sphere route (Table 1). Higher H₂O pressures favor the outer sphere routes and lead to lower χ values, because of a concomitant preference for H/OH⁺ over * species, as also evident from measured rin/rout ratios that decrease with increasing H₂O pressures (Fig. 4). High operating temperatures with low H₂O contents favor OO*-mediated inner sphere routes and thus lead to larger ratios of epoxidation to ODH rates. The χ values (=rin/rout) are also influenced by the composition of oxide catalysts, with a greater preference for inner sphere routes on the more reducible Mo-V based POM clusters than on W-POM clusters [14]. Such effects of redox properties of oxides on inner and outer sphere O₂ activation transition states, and their concomitant influences on rate constant ratios (rin/rout; Eq. (11)) and χ values are the subject to on-going studies, the results of which will be published at a later time.

### Table 1

DFT-derived electronic energies (ΔEᵩ), enthalpies (ΔHᵩ), entropies (ΔSᵩ), and Gibb's free energies (ΔGᵇ) of the transition states for inner and outer sphere O₂ activation routes (steps 4a and 4b; Scheme 3) referenced to common H/OH⁺ and O₂(g) precursors on NH₄-POM. DFT-derived structures of transition states are shown in Fig. 6.

<table>
<thead>
<tr>
<th>Inner sphere route (steps 4a; Scheme 3)</th>
<th>Outer sphere route (step 4b; Scheme 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔEᵩ (kJ mol⁻¹)</td>
<td>141</td>
</tr>
<tr>
<td>ΔHᵩ (kJ mol⁻¹)</td>
<td>131 (134)</td>
</tr>
<tr>
<td>ΔSᵩ (J mol⁻¹ K⁻¹)</td>
<td>54 (9)</td>
</tr>
<tr>
<td>ΔGᵇ (kJ mol⁻¹)</td>
<td>107 (92)</td>
</tr>
</tbody>
</table>

_a At 0 K in vacuum, without zero-point vibrational energy corrections.
_b Determined at 453 K and 1 bar of gaseous molecules. Values inside and outside parentheses are calculated by removal of low-frequency vibrations and by their substitution with 0.7 of translations and rotations of O₂(g), respectively.

![Fig. 7](image_url)  
**Fig. 7.** DFT-derived χ values (χ = rin/rout; Eq. (11)) on NH₄-POM as a function reciprocal temperature at (a) 0.01 kPa H₂O and (b) 0.01 to 10 kPa H₂O. The dashed line in (a) represent values obtained by removing the contributions of low-frequency vibrational modes while the solid lines are obtained by substituting such contributions with a 0.7 fraction of translational and rotational degrees of freedom of O₂(g) (values in Table 1). Differences between χ values from these two treatments are shaded. The symbol (■) represents the measured χ value (0.01 kPa H₂O, 453 K) determined by regressing the rate data in Figs. 3 and 9 to the functional form of the rate equation in Scheme 4. The shaded region in (b) represents χ values less than unity.

3.4. Effects of the concentrations of reduced centers on re-oxidation routes

The relative contributions from inner and outer sphere O₂ activation routes (steps 4a and 4b; Scheme 3) do not depend on the
**CH₂OH ODH rate equation**

\[
k'_{\text{ODH}} = \frac{k_{\text{ODH,OO}} P_{\text{CH₂OH}} + k_{\text{ODH,OO}} P_{\text{CH₂OH}} + k_{\text{Epox}} P_{\text{C₂H₆}}}{1 + \frac{k_{\text{out}}}{2k_{\text{out}} P_{O_2}}} \frac{k_{\text{in}}}{1 + \alpha (k_{\text{ODH,OO}} P_{\text{CH₂OH}})} \]

\[
\gamma = \frac{r_{\text{fast}}}{r_{\text{slow}}} = \frac{k_{\text{in}} P_{\text{H₂O}}[\text{HOO}⁺]}{k_{\text{out}} P_{\text{H₂O}}[\text{HOO}⁺]}
\]

**C₂H₆ epoxidation rate equation**

\[
k'_{\text{Epox}} = \frac{k_{\text{Epox}} P_{\text{C₂H₆}}}{1 + \frac{k_{\text{ODH,OO}} P_{\text{CH₂OH}} + k_{\text{Epox}} P_{\text{C₂H₆}}}{2k_{\text{out}} P_{O_2}}} \left(\frac{k_{\text{in}}}{k_{\text{in}} + \alpha k_{\text{ODH,OO}} P_{\text{CH₂OH}}}ight) \]

**Estimated rate parameters**

\[
K_{\text{CH₂OH}} = 0.21 \pm 0.06 \text{ kPa}^{-1}
\]

\[
k_{\text{ODH}} = 0.39 \pm 0.05 \text{ (kPa-ks-PO) }^{-1}
\]

\[
k_{\text{out}} = 1.1 \pm 0.5 \text{ (kPa-ks-PO) }^{-1}
\]

\[
k_{\text{Epox}} = 0.003 (\pm 0.004) \text{ kPa}^{-1}
\]

\[
\alpha = \frac{k_{\text{slow}}}{k_{\text{fast}}} = 3000 \pm 1000
\]

\[
\beta = \frac{k_{\text{Epox}}}{K_{\text{ODH,OO}}} = 0.3 \pm 0.05
\]

Scheme 4. Rate equations for CH₂OH ODH and C₂H₆ epoxidation derived from steps proposed in Schemes 2 and 3 and rate parameters estimated from measured data on NH₄-POM at 453 K. Details of the derivations are in Section S10. Rate parameters are estimated by fitting the rate data in Figs. 3 and 9 to the functional form of rate equations for C₂H₆ epoxidation and CH₂OH ODH. Uncertainties reflect 95% confidence intervals.

The total number of reduced centers present during steady-state ODH catalysis because both routes require one reduced center (\(^*\) or H/\(\text{OH}\)) for O₂ activation (Eq. (11)). They depend only on the chemical state of these reduced centers, because \(\left[^*\right][\text{H/OH}^-]\) ratios and thus \(^*\) and \(\text{H/OH}^-\) concentrations are set by the equilibrium constant (\(K_w\); step 3; Scheme 3) and the prevalent \(\text{H}_2\text{O}\) pressure. The completion of re-oxidation steps by \(\text{O}_2\) during each ODH turnover, however, requires the ultimate consumption of these \(\text{O}_2\)-derived species (\(\text{OO}^*\) and \(\text{H}_2\text{O}_2\)) in subsequent re-oxidation steps.

\(\text{H}_2\text{O}_2\) species formed via outer sphere \(\text{O}_2\) activation routes (step 4b; Scheme 3) can desorb and react with another reduced (\(^*\) or \(\text{H}/\text{OH}^-\)) or oxidized (\(\text{O}^*\)) center in NH₄-POM clusters. Homogeneous \(\text{H}_2\text{O}_2\) decomposition rates are undetectable below 723 K [53] and thus do not contribute at the conditions used in this study. \(\text{H}_2\text{O}_2\) can react with either type of reduced centers (\(^*\) or \(\text{H}/\text{OH}^-\)) in NH₄-POM to form \(\text{H}_2\text{O}\) (one or two molecules from \(^*\) or \(\text{H}/\text{OH}^-\), respectively) and re-oxidize these centers by forming \(\text{O}^*\) species (step 6a; Scheme 3) [12]. The sequential re-oxidation events via steps 4b and 6a in Scheme 3 complete the four-electron oxidation of \(\text{H}_2\text{O}_2\) reactions with \(^*\), \(\text{H}/\text{OH}^-\) and \(\text{O}^*\) species, respectively (steps 6a and 6b; Scheme 3). The rate ratios, \(\gamma = r_{\text{fast}}/r_{\text{slow}}\), depend on the value of \(\alpha = k_{\text{slow}}/k_{\text{fast}}\) and on \([\text{H}/\text{OH}^-]/[\text{O}^*]\) ratios. When the contributions by \(\text{OO}^*\)-mediated routes to re-oxidation events are minor, \(\text{H}/\text{OH}^-/[\text{O}^*]\) ratios are given by (derived derivation in Section S10):

\[
\gamma = \frac{r_{\text{fast}}}{r_{\text{slow}}} = \frac{k_{\text{in}} P_{\text{H}_2\text{O}}[\text{H}_2\text{O}_2^+]}{k_{\text{out}} P_{\text{H}_2\text{O}}[\text{H}_2\text{O}_2^+]} = \frac{k_{\text{slow}}}{k_{\text{fast}}}[\text{H}/\text{OH}^-]/[\text{O}^*]
\]

which applies, in general, for ODH reactions of different alkanols. The factor of two in the denominator reflects the two reduced centers that are re-oxidized by each \(\text{O}_2\). The \(K_{\text{ODH}}\) values depend on the free energy of a kinetically-relevant H-abstraction TS respect to its gaseous alkanol and \(\text{O}^*\) precursors. The substitution of Eq. (13) into Eq. (12) gives a value for \(\gamma = r_{\text{fast}}/r_{\text{slow}}\):

\[
\gamma = \frac{r_{\text{fast}}}{r_{\text{slow}}} = \frac{k_{\text{in}} P_{\text{H}_2\text{O}}[\text{H}_2\text{O}_2^+]}{k_{\text{out}} P_{\text{H}_2\text{O}}[\text{H}_2\text{O}_2^+]} = \frac{2K_{\text{OO}^*} P_{\text{alkanol}}}{K_{\text{out}} P_{\text{O}_2}}
\]

Next, we vary these \(\gamma\) values by using more reactive alkanols (C₃H₆OH; larger \(K_{\text{ODH}}\) value) and different CH₂OH/O₂ reactant ratio.

### 3.4.1. Effects of alkanol reactivity on ODH and C₃H₆ epoxidation rates

Alkanol ODH and C₃H₆ epoxidation rates, measured with two different alkanols (C₂H₅OH and CH₃OH), are shown in Fig. 8a at different C₃H₆ pressures (1–35 kPa; 453 K). C₃H₆OH/O₂ reaction rates were about three-fold larger than for CH₃OH, as expected from the weaker C–H bonds in C₂H₅OH [10,54]. Epoxidation rates approached constant asymptotic values with increasing C₃H₆ pressure for both alkanols, but these values were larger for C₂H₅OH than CH₃OH. These trends reflect higher \(\text{OO}^*\) formation rates.
resulting from a higher concentration of reduced centers (* and H/OH*) for the alkanol with larger ODH rate constant ($k_{\text{ODH}}$; Eq. (13)). Asymptotic epoxidation rates are much smaller than ODH rates for both alkanols, indicating that re-oxidation routes that exclude OO* intermediates remain the predominant re-oxidation path for both reactants. These asymptotic $r_{\text{Epox}}/r_{\text{ODH}}$ ratios reflect the fraction of re-oxidation events mediated by OO* intermediates, either via inner sphere O$_2$ activation or via H$_2$O$_2$ (formed in outer sphere routes) reactions with O$. C_2H_5OH$ reductants, which lead to larger coverages of reduced centers than CH$_3OH$, led to smaller $r_{\text{Epox}}/r_{\text{ODH}}$ ratios and to the less prevalent involvement of OO*-mediated routes (Fig. 8b). These data indicate that more abundant reduced centers (* or H/OH*) lead to a higher probability of H$_2$O$_2$ reactions with such centers, thus forming O$, instead of reacting with O$ to form OO* (steps 6a and 6b; Scheme 3), leading to the higher $c$ values observed for the more reactive alkanol (Eq. (14)).

3.4.2. Effects of CH$_3$OH and O$_2$ pressures on CH$_3$OH ODH and C$_3$H$_6$ epoxidation rates

Both CH$_3$OH ODH and C$_3$H$_6$ epoxidation rates increased with increasing CH$_3$OH pressure (<1 kPa; Fig. 9a), because reduced centers formed via CH$_3$OH dehydrogenation (step 2; Scheme 2) act as intermediates for epoxidation events by activating O$_2$ as OO$ species. The ($r_{\text{Epox}}/r_{\text{ODH}}$) ratios decreased with increasing CH$_3$OH pressure (Fig. 10), indicating that OO*-mediated re-oxidation routes become less prevalent as the concentration of reduced centers (* or H/OH*) increases. As in the case of the
more reactive alkanol, this reflects H2O2 reactions with reduced centers (* or H/OH*), which circumvent OO* formation via H2O2 reactions with O*.

The number of reduced centers also increases as the O2 pressure decreases (Eq. (13)). Epoxidation rates increased slightly with O2 pressure, even though ODH rates remained unchanged (Fig. 9b). These trends are evident in (rEpox/rODH) ratios that decreased monotonically with the reciprocal of O2 pressures (Fig. 10), indicative of a concomitant increase in γ values (Eq. (14)).

The effects of alkanol reactivity and CH3OH/O2 ratios on (rEpox/rODH) values indicate that H2O2 formed via outer sphere O2 activation routes react with reduced or oxidized centers (steps 6a and 6b; Scheme 3) at rates proportional to the relative concentrations of these centers (Eqs. (12)–(14)). These steps are mediated by the diffusive shuttling of H2O2(g), which allows the second two-electron oxidation to occur at reduced or oxidized centers present beyond molecular distances. In contrast, bound peroxy (OO*) species can access non-vicinal reduced centers only via the activated migration of one of its O-atoms throughout oxide surfaces; such OO* hopping routes, however, impose significant kinetic hurdles. As a result, they cannot account for the fast nature of re-oxidation routes during ODH turnovers. OO* species can decompose instead by two-electron oxidation of a gaseous reductant, either an alkanol (step 5a; Scheme 3) or an alkene (step 5b; Scheme 3), thus completing the four-electron oxidation by O2. In what follows, theoretical treatments are used to examine the routes by which O2-derived species (OO* or H2O2) react in subsequent steps to complete the reduction-oxidation cycles required for catalytic oxidation turnovers.

3.5. DFT-derived free energies of intermediates and transition states involved in the reactions of O2-derived species

3.5.1. Decomposition routes of bound peroxy (OO*) species

3.5.1.1. OO* reactions with a distant reduced center. During ODH catalysis, reduced centers are present as minor species, as evidenced from the zero-order dependence of ODH rates on O2 pressure (Figs. 1b and 3b) and from in-situ UV–vis studies [19]. The unfavorable thermodynamics also lead these centers (i.e. O-vacancies) to be isolated, consistent with much higher energy (by 117 kJ mol\(^{-1}\)) of the H-POM cluster with vicinal O-vacancies than with isolated O-vacancies (located at Ob2 and Ob3 versus Ob2 and Ob4; Fig. S11). This is also evident from DFT-derived HAE values, which become much less negative (by ~50–70 kJ mol\(^{-1}\)) for O-atoms near a reduced center (H/OH*) than for distant O-atoms, indicative of the unlikely formation of proximal reduced centers (Fig. S11). The decomposition of bound peroxy (OO*) species via reactions with another reduced center (OO* + * = \(20\)) thus requires sequential “OO* hopping” steps to reach a non-vicinal reduced center, where the migrating species must traverse significant distances at such low prevalent concentrations of reduced centers. Fig. 11 shows DFT-derived free energies (453 K, 1 bar) and the structures of the intermediates and transition states involved in OO* decomposition via hopping to non-vicinal reduced center. Free energies are referenced to OO* and non-vicinal H/OH*, which represent the “reactants” in such migration events.

An O-vacancy (*) forms from H/OH* species via recombinative desorption of H2O (step 3; Scheme 2; Section 3.3.2). The reaction of this vacancy with non-vicinal OO* must involve a migration of an O-atom in OO* to a vicinal O*. This O-hopping step involves a TS (TS\(_{\text{hop}}\); Fig. 11a) that represents the highest barrier (\(\Delta G^f = 151\) kJ mol\(^{-1}\)) along the OO* decomposition reaction coordinate; this step must occur several times in order to reach a remote vacancy. Once OO* reaches a location vicinal to * (OO*: Fig. 11b), it reacts to form two O* species via a TS (TS\(_{\text{react}:\text{OO*}}\); Fig. 11c) with a free energy barrier much lower than the O-hopping step.

DFT-derived activation barriers for OO* hopping steps (\(\Delta G^f = 151\) kJ mol\(^{-1}\)) are much higher than OO* formation steps via either via another reduced center or outer sphere O2 activation routes (steps 3a, 4a and 4b; Scheme 3; 107 and 78 kJ mol\(^{-1}\); Section 3.3.2). These barriers are also higher than the kinetically-relevant H-abstraction step (step 2; Scheme 2; 139 kJ mol\(^{-1}\)) and thus inconsistent with re-oxidation rate constants that are much larger than for reduction steps [19], and with the presence of reduced centers as minority species during ODH reactions. Therefore, we conclude that OO* migrations and reactions with another reduced center do not contribute detectably to re-oxidation events in Mars-van Krevelen redox cycles for these oxide systems.

3.5.1.2. OO* reactions with alkanols. The dearth of vicinal reduced centers and the high OO* hopping barriers indicate that more facile OO* decomposition routes must be involved. OO* can react with reactant alkanols to form alkanals and H2O, regenerating O* (step 5a; Scheme 3). Fig. 12 shows DFT-derived structures and free energies (453 K, 1 bar) of intermediates and transition states involved in such routes.

CH\(_3\)OH adsorbs weakly on OO* (\(\Delta G = 4\) kJ mol\(^{-1}\); Fig. 12a) and reacts via a C–H activation TS (TS\(_{\text{Dehyd}:\text{CH}_3\text{OH}}\); Fig. 12b) with a free energy of 94 kJ mol\(^{-1}\), referenced to its CH\(_2\)OH(g) and OO* precursors. This C–H activation can lead to OH* and a bound CH\(_2\)OH species, which forms HCHO (Fig. 12c) via a sequential O–H activation step by a vicinal O*; the free energy of this O–H cleavage TS (\(\Delta G^f = 14\) kJ mol\(^{-1}\), referenced to CH\(_3\)OH(g) and OO*; Fig. S12) is much lower than the C–H activation TS. The OO* species and vicinal OH* formed react to release H2O and re-form O* via a dehydration TS (TS\(_{\text{Dehyd}}\); Fig. 12d), which also present much lower activation barrier than the C–H activation step. Alternatively, the C–H activation can be followed by an insertion of an O-atom in OO* into the C–H bond in CH\(_2\)OH to form methane diol (Fig. 12e), which dehydrates to form HCHO and H2O via a H-atom transfer TS (TS\(_{\text{Dehyd}2}\); Fig. 12f) with a free energy much lower
Fig. 11. DFT-derived free energies (kJ mol\(^{-1}\); 453 K, 1 bar) and structures of intermediates and transition states involved in OO* decomposition routes on NH₄-POM via O-atom migration and reaction with another reduced center. Free energies of OO* and H/OH* are taken as reference.

Fig. 12. DFT-derived free energies (kJ mol\(^{-1}\); 453 K, 1 bar) and structures of intermediates and transition states on NH₄-POM involved in OO* reactions with \(\text{CH}_3\text{OH}(g)\) to form \(\text{O}^*\), HCHO\((g)\) and \(\text{H}_2\text{O}(g)\) (step 5a; Scheme 3). Two plausible reaction routes, one involving sequential C-H activation and O-H activation and another inserting O-atom into C-H bond are considered. Free energies of OO* and \(\text{CH}_3\text{OH}(g)\) are taken as reference.
than the C–H activation TS. In both cases, OO* decomposes to reform \( \text{O}^- \) by reacting with CH\(_3\)OH(g), ultimately leading to form HCHO and H\(_2\)O.

The ratio of the rates for OO* decomposition via oxidation of non-vicinal reduced centers (\(^*\)) to that for its oxidation of CH\(_3\)OH (g) reactants (\( \delta = \frac{r_{\text{OO}}}{r_{\text{ODH,OO}}} \)) is given by:

\[
\delta = \frac{r_{\text{OO}}}{r_{\text{ODH,OO}}} = \frac{k_{\text{Epox}}(\text{OO}^*|\text{H}/\text{OH}^*o)}{k_{\text{Epox}}(\text{CH}3\text{OH}|\text{CH}3\text{OH})}
\]

Here, \( k_{\text{ODH,OO}} \) reflects the first-order rate constant for OO* reaction with CH\(_3\)OH(g) and depends on the free energy of a C–H activation TS (TS\(_{\text{ODH,OO}}\); Fig. 12b), relative to its CH\(_3\)OH(g) and OO* precursors. \( k_{\text{ODH,OO}} \) is the rate parameter for OO* reaction (step 5b; Scheme 3), which reflects the free energy of an O-insertion TS (TS\(_{\text{ODH,OO}}\); Fig. 13b), referenced to CH\(_3\)OH(g) and OO*. The value of \( \delta \) \( = k_{\text{Epox}}/k_{\text{ODH,OO}} \) derived from DFT calculations (0.12) is smaller than unity, indicating that equimolar CH\(_3\)H\(_2\)-CH\(_3\)OH reactants would preferentially decompose OO* via reactions with CH\(_3\)OH instead of CH\(_3\)H\(_2\). Such conclusions are consistent with epoxidation rates that increase with increasing CH\(_3\)H\(_2\) pressure and reach constant values only for CH\(_3\)H\(_2\)/CH\(_3\)OH ratios much larger than unity (Fig. 3a).

These OO*-mediated routes account for only a small fraction (<0.1) of all re-oxidation events during CH\(_3\)OHDH on NH\(_4\)-POM clusters, as shown by asymptotic (\( r_{\text{Epox}}/r_{\text{ODH}} \)) ratios much smaller than unity (<0.1; Fig. 4). The alternate and predominant routes mediated by H\(_2\)O molecules are discussed next.

3.5.2.1. \( \text{H}_2\text{O}_2 \) reactions with reduced centers. H\(_2\)O\(_2\) molecules formed via outer sphere O\(_2\) activation at H/OH* species (step 4b; Scheme 3) can re-oxidize another reduced center (\(^*\) or H/OH*) to re-form O\* (step 6a; Scheme 3), thus acting as the O-atom shuttle between two reduced centers located beyond molecular distances. Fig. 14 shows DFT-derived free energies (453 K, 1 bar) and structures for the intermediates and transition states that mediate these H\(_2\)O\(_2\) decomposition on \(^*\) or H/OH*. Free energies in both cases are referenced to H\(_2\)O\(_2\)(g) and H/OH* species to allow a rigorous comparison based on their rate ratios.

H\(_2\)O\(_2\) decomposition on O-vacancies (\(^*\)) involves molecular adsorption of H\(_2\)O\(_2\) (\( \Delta G_{\text{ads}} = -3 \text{ kJ/mol} \); \(^*\)H\(_2\)O\(_2\); Fig. 14a) and reactions with a vicinal O* via a H-transfer TS (\( \Delta G = 70 \text{ kJ mol}^{-1} \), referenced to H\(_2\)O\(_2\)(g) and H/OH*; TS\(_{\text{ad}}\); Fig. 14b) to form vicinal OOH* and OH* (OOH/H*; Fig. 14c). These two species then recombine to form H\(_2\)O(g) and O* via a H\(_2\)O elimination TS (TS\(_{\text{dehyd}}\); Fig. 14d) with a free energy much less than TS\(_{\text{ad}}\).

The decomposition of H\(_2\)O\(_2\) on H/OH* without intervening vacancy formation involves weak H\(_2\)O\(_2\) adsorption (\( \Delta G_{\text{ads}} = 35 \text{ kJ mol}^{-1} \}; H/OH*/H\(_2\)O\(_2\); Fig. 14e) and a TS (\( \Delta G = 84 \text{ kJ mol}^{-1} \), referenced to H\(_2\)O\(_2\)(g) and H/OH*; TS\(_{\text{ad}}\); Fig. 14f) that leads to form two adsorbed H\(_2\)O molecules at vicinal O* species (O*\_2H\(_2\)O; Fig. 14g). This route avoids the formation or cleavage of Mo–O bonds, as in the case of outer sphere O\(_2\) activation on H/OH* species (step 4a; Scheme 3).

![Fig. 13. DFT-derived free energies (kJ mol\(^{-1}\); 453 K, 1 bar) and structures of intermediates and transition states on NH\(_4\)-POM involved in OO* reactions with C\(_3\)H\(_6\) to form O* and propene oxide (step 5b; Scheme 3). Free energies of OO* and C\(_3\)H\(_6\)(g) are taken as reference.](image-url)
The relative rates for H$_2$O$_2$ reactions with * and H/OH* depend on the ratios of their rate constants and on the relative abundance of two centers; the ([*]/[H/OH]) ratio is determined by the water adsorption equilibrium constant on * (K$_w$) and the H$_2$O pressure. H$_2$O$_2$ reactions with * and H/OH* ultimately re-oxidize one reduced center to form O*, thus completing a four-electron re-oxidation using one O$_2$ molecule without involving OO* intermediates; these two H$_2$O$_2$ decomposition routes are shown together as step 6a in Scheme 3.

3.5.2.2. H$_2$O$_2$ reactions with O* and the kinetic crossing between outer and inner sphere O$_2$ activation routes.

DFT-derived free energies (453 K; 1 bar) and structures of intermediates and transition states involved in H$_2$O$_2$ reactions with O* to form OO* and H$_2$O (step 6b; Scheme 3) are shown in Fig. 15. Weakly-adsorbed H$_2$O$_2$ on O* ($\Delta G_{ads} = 10 \text{ kJ mol}^{-1}$; O*-H$_2$O$_2$; Fig. 15a) forms vicinal hydroperoxo (O-OOH) and OH* (denoted as O-OOH/H*; Fig. 15c) species in a step mediated by a TS in which one H-atom is abstracted from H$_2$O$_2$ by O* (TS$_{6b_1}$; Fig. 15b). The free energy barrier is 140 kJ mol$^{-1}$ when referenced to H$_2$O$_2$(g) and O*. These O-OOH/H* species form bound peroxo species (OO*) and H$_2$O via an O-insertion TS (TS$_{6b_2}$; Fig. 15d) with a free energy barrier of 158 kJ mol$^{-1}$ (referenced to H$_2$O$_2$(g) and O*), which exhibits the highest free energy along the reaction coordinate. This route creates a kinetic shunt between inner and outer sphere O$_2$ activation routes through the formation of OO* species, typically associated with inner sphere routes (step 4a; Scheme 3), using the reaction of H$_2$O$_2$, formed in outer sphere routes (step 4b; Scheme 3), with O* (step 6b; Scheme 3). Such kinetic shunt leads, in turn, to an increase in ($r_{Epox}$/r$_{ODH}$) ratios as reduced centers become less prevalent and H$_2$O$_2$ preferentially react with O* to form OO* species required for epoxidation events (Section 3.4).

Asymptotic $r_{Epox}$/r$_{ODH}$ ratios much smaller than unity (<0.1; Fig. 4) reflect the minor contributions by OO* -mediated routes to re-oxidation events at typical ODH conditions. This suggests, in turn, that the H$_2$O$_2$ molecules formed in the predominant O$_2$ activation route (step 4a; Scheme 3) react predominantly with reduced centers (* or H/OH*) instead of with O*, even when re-oxidation events are facile and reduced centers are present as minority species during ODH catalysis. Indeed, DFT-derived free energy barriers for H$_2$O$_2$ reactions with O* to form OO* (156 kJ mol$^{-1}$) are much higher than for H$_2$O$_2$ reactions with * (70 kJ mol$^{-1}$) or H/OH* (84 kJ mol$^{-1}$) to form O* and H$_2$O, when referenced to the same H$_2$O$_2$(g) precursor and to the respective surface species (O* or H/OH*).

The OO* species involved in epoxidation events are formed via inner sphere O$_2$ activation (step 4a; Scheme 3) and via outer sphere O$_2$ activation and successive H$_2$O$_2$ reactions with O* (steps 4b and
A preference for OOO*-mediated re-oxidation routes is required for high epoxidation selectivities during ODH reactions, which can be achieved by increasing $r_{6a}/r_{6b}$ ratios ($\chi$: Eq. (11)) and decreasing $r_{od}/r_{out}$ ratios ($\gamma$: Eq. (14)). An increase in $r_{6a}/r_{6b}$ ratios ($\chi$: Eq. (11)) leads to a larger fraction of reduced centers forming to OOO* species (instead of H$_2$O$_2$) and can be achieved by operating at higher temperatures or lower H$_2$O contents (Section 3.3.3). A decrease in $r_{6a}/r_{6b}$ ratios ($\gamma$: Eq. (14)) also leads to a greater preference for OOO*-mediated routes by increasing the fraction of H$_2$O$_2$ molecules reacting with O* to form OOO* species (and H$_2$O). Lower $\gamma$ and H/OH* coverages minimize H$_2$O$_2$ decomposition on such centers and lead to the higher ($r_{od}/r_{out}$) ratios observed for less reactive alkane and CH$_3$OH/O$_2$ ratios (Eq. (14)).

### 3.6. Kinetic rate equations for CH$_3$OH ODH and C$_3$H$_6$ epoxidation

Schemes 2 and 3 summarize plausible routes for the reduction and re-oxidation parts of ODH cycles and for the scavenging reactions of OOO* intermediates via C$_3$H$_6$ epoxidation. The rate equations for CH$_3$OH ODH and C$_3$H$_6$ epoxidation are derived here, in order to compare their consistency with kinetic data in Figs. 3 and 9 and to estimate rate parameters for the elementary steps.

The steps in Schemes 2 and 3, taken together with the assumptions about their reversibility, discussed in detail in the previous sections, lead to rate equations for CH$_3$OH ODH and C$_3$H$_6$ epoxidation (listed in Scheme 4). The derivation of the rate equations is discussed here. Steps 2 (Scheme 2) and 5a (Scheme 3) both form ODH products, leading to a combined ODH rate ($r_{ODH}$) given by:

$$r_{ODH} = k'_{ODH}P_{CH}O_{OH}[O'^*] + k_{ODH,OO*}P_{CH}O_{OH}[OO'^*]$$  \hspace{1cm} (17)

$k'_{ODH}$ and $k_{ODH,OO*}$ denote first-order rate constants for step 2 (Scheme 2) and step 5a (Scheme 3), respectively. C$_3$H$_6$ epoxidation rates ($r_{epox}$) depend on the rate constant ($k_{epox}$) for step 5b (Scheme 3), the C$_3$H$_6$ pressure, and the concentration of OOO* species (Eq. (6)). The steady-state [OO*] concentration is given by (derivation in Section S10):

$$[OO*] = \frac{k_{epox}P_{CH}O_{OH}[OO'^*]}{k_{ODH,OO*}P_{CH}O_{OH} + k_{epox}P_{CH}H_2} [O'^*].$$  \hspace{1cm} (18)

for the case of re-oxidation predominantly mediated via steps 4b and 6a (Scheme 3), as is evident from the small asymptotic $r_{epox}/r_{ODH}$ values at high C$_3$H$_6$/CH$_3$OH ratios (Fig. 4). Here, $K_W$ denotes the equilibrium constant for step 3 (Scheme 3) and $k_{in}$ and $k_{out}$ are the first-order rate constants for inner and outer sphere O$_2$ activation (steps 4a and 4b; Scheme 3). The ratio of rate constants for H$_2$O$_2$ reactions with reduced and oxidized centers is given by $\alpha$ (Eq. (12)). When reduced centers and bound O$_2$-derived species are present as minority surface species, the site balance gives an expression for [O*]:

$$[O'^*] = \frac{1}{1 + K_{CH}O_{OH}P_{CH}O_{OH} + K_{H_2}O_P_{CH}H_2 + K_{CH}H_2P_{CH}H_2}$$  \hspace{1cm} (19)

The denominator terms reflect the relative surface concentrations of (O'), (CH$_3$OH-O'), (H$_2$O-O'), (C$_3$H$_6$-O'), in the order that they appear.

The substitution of Eqs. (18) and (19) into Eqs. (17) and (6) leads to ODH and epoxidation rate equations (Scheme 4). The regression of the kinetic data in Figs. 3 and 9 to the functional form of these rate equations gives the groups of equilibrium and rate constants listed in Scheme 4. These CH$_3$OH ODH and C$_3$H$_6$ epoxidation rate equations accurately describe all rate data, as shown by the dashed curves in Figs. 3 and 9. Parity plots for ODH and epoxidation rates are shown in Fig. S13. Without C$_3$H$_6$ co-reactants, the CH$_3$OH ODH rate equation (Scheme 4) simplifies to Eq. (5) when re-oxidation events predominantly occur via steps 4b and 6a (Scheme 3).

### 4. Conclusions

C$_3$H$_6$ molecules are used to scavenge bound O$_2$-derived species formed during the re-oxidation part of Mars-van Krevelen catalytic cycles for alkane ODH on solid oxides. The effects of C$_3$H$_6$, H$_2$O, CH$_3$OH, and O$_2$ pressures and the reactivity of alkane on alkane ODH and C$_3$H$_6$ epoxidation rates and their rate ratios are analyzed to provide insights on kinetic networks and elementary steps involved in re-oxidation routes and on the involvement of O$_2$-derived species for O-insertion reactions. Such experiments are combined with DFT treatments of free energies of relevant intermediates and transition states to address the types of O$_2$-derived species mediating re-oxidation routes and the relative rates of their formations and decompositions.

C$_3$H$_6$ epoxidation products are detected in O$_2$-C$_3$H$_6$ mixtures only when alkane are also present in reactant streams and they undergo ODH reactions. Such coupling of ODH and epoxidation reactions suggests that reduced centers formed via alkane ODH act as reactants for O$_2$ activation that leads to the formation of...
electrophilic dioxygen species required for epoxidation. These mechanistic interpretations are consistent with inner sphere O₂ activation routes mediated by bound peroxy (OO’⁠) species, which are ubiquitous in homogeneous POM catalysis, electro-catalysis and bio-catalysis with monooxygenase enzymes. The contributions of these OO’-mediated routes to re-oxidation events, however, are minor for Mo-based NH₄-POM clusters, as evidenced by epoxidation to ODH rate ratios that were much less than unity (<0.1) at all relevant conditions.

The alternative and predominant re-oxidation routes involve proton-coupled electron-transfers from reduced centers (H/ØH⁠) to O₂ to form H₂O₂, which can easily desorb and re-oxidize another reduced center (‘or H/ØH⁠) to form O’⁠ (and H₂O). The H₂O₂ molecules can also react with an oxidized center (O’⁠) to form OO’⁠ species (and H₂O), creating a kinetic shunt between inner and outer sphere O₂ activation routes; this shunt leads to higher epoxidation to ODH rate ratios at lower reduced center concentrations.

Unlike H₂O₂ molecules, which can desorb and act as a molecular shuttle to carry extra O-atoms between surface species that present at distances larger than molecular dimensions, reactions of bound OO’⁠ species with non-vicinal reduced centers require kinetically demanding O-hopping steps that must occur several times to reach an O’ center vicinal to the reduced center. OO’⁠ species instead can react with a gas-phase reactant, alkanol (CH₃OH) and alkene (C₃H₆), to ultimately re-form O’⁠ and form ODH and epoxidation products; these routes present much lower activation barriers than conventional O-hopping mechanisms.

Kinetic analyses on the ODH and scavenging epoxidation reactions, and their seamless combination with DFT calculations of their elementary steps construct a general conceptual framework for the analysis of redox reactions that have been refractory to probes of re-oxidation mechanisms. In doing so, we show the re-oxidation routes that prefer molecular donor (H₂O₂) or acceptor (CH₃OH and C₃H₆) to perform sequential two-electron oxidation events occurring at distant locations, instead of the kinetically-demanding O-hopping routes. Epoxidation routes uncovered in this work also open possibilities of kinetically coupling two oxidation reactions, alkanol ODH and epoxidation, to utilize both of the O-atoms in O₂ molecule. Such routes, upon further optimization, may provide an economic process to perform epoxidation without requiring expensive oxidants, such as H₂O₂ and organic peroxides.

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Appendix A. Supplementary material

Reaction networks of alkanol-O₂ reactions on bifunctional catalysts; effects of NH₃ titrations of acid sites on CH₃OH dehydrogenation and ODH rates; time-on-stream CH₃OH dehydrogenation and ODH rates before and after introduction of C₃H₆ co-feed on H-POM; time-on-stream CH₃OH ODH, and C₃H₆ epoxidation rates on NH₄-POM; CH₃OH ODH product selectivities on NH₄-POM as a function of CH₃OH conversions; the values of rate and equilibrium constants for CH₄OH ODH, DFT-derived reactivity-averaged HAE, H-abstraction free energy barriers and CH₃OH adsorption free energy changes on H-POM and NH₄-POM; product selectivities of C₃H₆ conversions during CH₃OH-O₂-C₃H₆ reactions as a function of C₃H₆ conversions; effects of H₂O on CH₃OH ODH rates; acetone formation rates from O₂-C₃H₆-H₂O reactions on NH₄-POM; C₃H₆ conversion and epoxidation rates from CH₃OH-O₂-C₃H₆-H₂O reactions on NH₄-POM; spin density maps for the OOH intermediate; DFT-derived structures of transition states involved in outer sphere O₂ activation routes; DFT-derived HAE on two-electron reduced H-POM cluster; DFT-derived structures of transition states involved in reactions of OO* with CH₃OH; DFT-derived entropies, enthalpies, and Gibbs free energies for intermediates and transition states involved re-oxidation steps in Scheme 3; derivations of rate equations for CH₃OH ODH and C₃H₆ epoxidation; a comparison of CH₃OH ODH and C₃H₆ epoxidation rates from the model and experiment. Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.jcat.2018.05.016.

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