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# 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\*) or H<sub>2</sub>O<sub>2</sub> species, denoted as innersphere and outer-sphere routes respectively, for metal-oxo catalysts solvated by liquids. On solid oxides, O<sub>2</sub> 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\* species with C<sub>3</sub>H<sub>6</sub> to form epoxides and by energies and barriers from density functional theory. Alkanols react with O-atoms ( $O^*$ ) in oxides to form vicinal OH pairs that eliminate  $H_2O$  to form  $OO^*$  at O-vacancies formed or react with  $O_2$  to give  $H_2O_2$ .  $OO^*$  reacts with alkanols to re-form  $O^*$  via steps favored over OO<sup>\*</sup> migrations, otherwise required to oxidize non-vicinal vacancies.  $C_3H_6$  epoxidizes by reaction with OO\* with rates that increase with C<sub>3</sub>H<sub>6</sub> pressure, but reach constant values as all OO\* species react with C<sub>3</sub>H<sub>6</sub> at high C<sub>3</sub>H<sub>6</sub>/alkanol ratios. Asymptotic epoxidation/ODH rate ratios are smaller than unity, because outer-sphere routes that shuttle O-atoms via  $H_2O_2(g)$  are favored over endoergic vacancy formation required for inner-sphere routes. The relative contributions of these two routes are influenced by H<sub>2</sub>O, because vacancies, required to form OO\*, react with H<sub>2</sub>O to form OH pairs and H<sub>2</sub>O<sub>2</sub>. OO\*mediated routes and epoxidation become favored at low coverages of reduced centers, prevalent for less reactive alkanols and lower alkanol/O2 ratios, because H2O2 then reacts preferentially with O\* (forming  $OO^*$ ), instead of vacancies (forming  $O^*/H_2O$ ). Such kinetic shunts between two routes compensate for lower barriers required to form H<sub>2</sub>O<sub>2</sub> than OO\*. These re-oxidation routes prefer molecular donor (H<sub>2</sub>O<sub>2</sub>) 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.

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## 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

\* Corresponding author. *E-mail address: iglesia@berkeley.edu* (E. Iglesia). lattice O-atoms (O<sup>\*</sup>) 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<sup>\*</sup>), which can dehydroxylate and lead to reduced centers in the form of O-vacancies (\*) in the oxide lattice; both types of reduced centers can react with O<sub>2</sub> to re-form oxidized centers (O<sup>\*</sup>), 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<sub>2</sub>-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 electrocatalysis [12–14] and monooxygenase enzyme systems [15–18],









**Scheme 1.** A Mars-van Krevelen redox cycle involving the reduction of lattice O-atoms ( $O^*$ ) in Mo-based oxide domains via alkanol dehydrogenation steps and re-oxidation of reduced centers ( $H/OH^*$ ) via  $O_2$  activation steps.

which use activated forms of O<sub>2</sub>-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 UVvisible spectra during the transient formation and consumption of reduced centers in response to changes in reductant to oxidant ratios in the reactant streams [19]. Previous studies of propane ODH on supported VO<sub>x</sub>-based catalysts indicate that re-oxidation first-order rate constants are 10<sup>3</sup>-10<sup>5</sup> times larger than for the kinetically-relevant reduction steps [19]; as a result, reduced centers are present as minority species during ODH catalysis, consistent with the observed insensitivity of ODH rates to O<sub>2</sub> 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 reoxidation by a four-electron oxidant such as O<sub>2</sub> thus requires the kinetic coupling of two elementary events, each involving one Oatom (and two electrons). Such coupling requires, in turn, the migration of one of the O-atoms in O<sub>2</sub>, either 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 (OO<sup>\*</sup>) intermediates formed via O<sub>2</sub> activation at Ovacancies (\*) with concurrent two-electron re-oxidation of the reduced centers [11,20]. Several sequential diffusional hops by one O-atom in the OO<sup>\*</sup> intermediates formed can bring OO<sup>\*</sup> species near another O-vacancy (\*) and re-oxidize the reduced center (\*) to form another lattice O-atom (O<sup>\*</sup>), thus completing the required four-electron re-oxidation process using O<sub>2</sub> [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 (OO<sup>\*</sup>) species exhibit detectable UV-visible [23] and Raman [24] features that have been detected during the re-oxidation of reduced CeO<sub>2</sub>-based solids by O<sub>2</sub>. The detection of bound OO<sup>\*</sup> 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"  $O_2$  activation mechanism circumvents the need for M—O bond cleavage by effecting re-oxidation through coupled proton-electron-transfer from reduced centers (H/OH<sup>\*</sup>) to  $O_2(g)$  to form  $H_2O_2$  [12,14,26,27]. Such routes lead to

the appearance of the <sup>17</sup>O-atoms in <sup>17</sup>O<sub>2</sub>(g) within H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O molecules, but not in W—O bonds, during the re-oxidation of aqueous W-polyoxometalate anions [14]. The relative contributions of inner and outer O<sub>2</sub> activation routes are quite consequential for alkane ODH selectivity because peroxo (OO<sup>\*</sup>) intermediates, involved in inner sphere O<sub>2</sub> activation routes, can mediate O-insertion reactions and convert primary alkene products to reactive epoxides that can undergo fast subsequent oxidation to CO and CO<sub>2</sub> [10,11,28,29]. The involvement of OO<sup>\*</sup> species in the reoxidation 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 reoxidation of reduced Mo-based Keggin-type polyoxometalate (POM) clusters and for the presence of OO<sup>\*</sup> 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  $OO^*$  species with  $C_3H_6$  during alkanol ODH catalysis and by density functional theory (DFT) treatments of the relevant intermediates and transition states. Mobased 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 redox active metal oxides that involve parallel inner and outer sphere O<sub>2</sub> activation routes. CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH 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 OO<sup>\*</sup> 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 H<sub>2</sub>O<sub>2</sub> molecules that convert to  $H_2O$  as a sacrificial reaction [29,31].

#### 2. Methods

#### 2.1. Experimental methods

Supported Mo-based Keggin-type POM clusters ( $H_3PMo_{12}O_{40}$ ) were prepared by incipient wetness method using SiO<sub>2</sub> (Cab-O-Sil; 304 m<sup>2</sup> g<sup>-1</sup>; 1.5 cm<sup>3</sup> g<sup>-1</sup> pore volume) as a mesoporous support. SiO<sub>2</sub> support was rinsed three times with 1 M HNO<sub>3</sub> (10 cm<sup>3</sup> g-SiO<sub>2</sub><sup>-1</sup>) to remove any impurities and then treated in flowing dry air (UHP Praxair, 0.83 cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>) at 383 K for 12 h and at 573 K for 5 h before impregnation with aqueous solutions of  $H_3PMo_{12}$ - $O_{40}$  (99.99%, Sigma-Aldrich) to give samples with 25.4% wt. POM, corresponding to a surface density of 0.4 POM nm<sup>-2</sup>. Impregnated samples were kept in closed vials at ambient temperature for 24 h and then treated in flowing He (99.999%, Praxair, 0.83 cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>) at 323 K for 24 h. The powders were then pressed into pellets, crushed, and sieved to retain 106–180 µm aggregates. Transmission electron microscopy showed that POM clusters after synthesis (and also after CH<sub>3</sub>OH ODH reactions) were predominantly present

as isolated clusters with two-dimensional structures present only as minority species [3]; their intact Keggin structure was confirmed by <sup>31</sup>P NMR [3].

 $C_3H_6$  and  $CH_3OH$  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<sub>2</sub> (99.999% or 25% O<sub>2</sub>/He, Praxair), He (99.999%, Praxair) and  $C_3H_6$  (99.95%, Praxair) were metered electronically by mass flow controllers (Porter Instrument) in order to maintain desired reactant concentrations and residence times. Liquid CH<sub>3</sub>OH (99.9%, Fisher Scientific), C<sub>2</sub>H<sub>5</sub>OH (99.5% anhydrous, Sigma-Aldrich), and H<sub>2</sub>O (doubly-distilled and deionized) were delivered to the reactant streams using syringe pumps (Cole Parmer, 60,061 Series) by vaporizing the liquids at 393 K into the flowing gas stream (O<sub>2</sub>/He or O<sub>2</sub>/He/C<sub>3</sub>H<sub>6</sub>).

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<sub>2</sub>-H<sub>2</sub>O (20 kPa O<sub>2</sub> and 2 kPa H<sub>2</sub>O; 0.8 cm<sup>3</sup> s<sup>-1</sup>) during temperature ramp (0.083 K s<sup>-1</sup>) 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 × 1.05 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  $(H_3PMo_{12}O_{40})$  clusters contain protons  $(H^+)$  that act as Brønsted acids and lattice O-atoms  $(O^*)$  that act as redox sites. Reactions of alkanols (CH<sub>3</sub>OH or C<sub>2</sub>H<sub>5</sub>OH) and O<sub>2</sub> 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<sub>3</sub> (1%, Praxair) at 453 K using NH<sub>3</sub>-pulses (4  $\mu$ mol per pulse; He as a carrier gas, 1.6 cm<sup>3</sup> s<sup>-1</sup>) during alkanol-O<sub>2</sub>-H<sub>2</sub>O reactions (4 kPa alkanol, 20 kPa  $O_2$ , 2 kPa  $H_2O$ ) 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<sub>3</sub> pulses were introduced until alkanol dehydration rates became undetectable (< 0.1% of initial rates), indicative of the essential removal of Brønsted acid sites. The changes in dehydration and dehydrogenation rates as a function of NH<sub>3</sub> doses are shown in Supporting Information (Fig. S1). These NH<sub>3</sub>-titrated samples were used for all alkanol-O<sub>2</sub> reactions with and without  $C_3H_6$  co-reactants after removal of all traces of  $NH_3(g)$  with He (1.6 cm<sup>3</sup> s<sup>-1</sup>) for 0.2 h. These samples are hereinafter denoted as NH<sub>4</sub>-POM. Dehydration rates on NH<sub>4</sub>-POM remained at nearly undetectable levels throughout all experiments, as expected from the strong binding of NH<sub>3</sub> at POM protons at 453 K. For comparison, CH<sub>3</sub>OH ODH rates were also measured on H-POM samples with acidic protons.

CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, and C<sub>3</sub>H<sub>6</sub> conversions were kept below 3% to maintain constant axial concentrations along the bed and to minimize any effects of the H<sub>2</sub>O formed on rates or selectivities. No conversion of alkanols or C<sub>3</sub>H<sub>6</sub> was detected on the SiO<sub>2</sub> support. No detectable amounts of CO and CO<sub>2</sub> were formed at any of the reaction conditions used. CH<sub>3</sub>OH ODH turnover rates (r<sub>ODH</sub>; per POM cluster) are defined as the sum of formaldehyde (HCHO), methylformate (MF) and dimethoxymethane (DMM) molar formation rates (r<sub>ODH</sub> = r<sub>HCHO</sub> + r<sub>MF</sub> + r<sub>DMM</sub>), 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<sub>4</sub>-POM remained high (> 60%) at typical reaction conditions (Fig. S2). Acetaldehyde was the only product of

C<sub>2</sub>H<sub>5</sub>OH ODH reactions and C<sub>2</sub>H<sub>5</sub>OH ODH rates are reported as acetaldehyde molar formation rates. C<sub>3</sub>H<sub>6</sub> epoxidation rates ( $r_{Epox}$ ; per POM cluster) are reported as the sum of the formation rates of propene epoxide (PE) and acetone (Ace) ( $r_{Epox} = r_{PE} + r_{Ace}$ ), because acetone is formed only via secondary isomerization of propene oxide [32] in the absence of co-fed H<sub>2</sub>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 valencecore 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 planewave 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<sup>-1</sup>.

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  $CH_3OH$  adsorption energies on  $O^*$ sites. The central P atom in each POM cluster was fixed to prevent net translation of structures, 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  $1 \times 10^{-5}$  eV and forces within 0.1 eV Å<sup>-1</sup>. 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<sup>-1</sup> 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)

$$G = E_0 + ZPVE + G_{vib} + G_{trans} + G_{rot}$$
<sup>(2)</sup>

Low-frequency modes (less than  $\sim$ 150 cm<sup>-1</sup>) 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;

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G^{\dagger}}{RT}\right) \tag{3}$$

where  $\Delta G^{\ddagger}$  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 ( $\Delta G^{\varnothing}$ );

$$K = \exp\left(\frac{-\Delta G^{\varnothing}}{RT}\right) \tag{4}$$

#### 3. Results and discussion

### 3.1. CH<sub>3</sub>OH-O<sub>2</sub> reactions on H-POM and NH<sub>4</sub>-POM

CH<sub>3</sub>OH ODH rates increased linearly with CH<sub>3</sub>OH pressure (<1 kPa CH<sub>3</sub>OH) on both H-POM and NH<sub>4</sub>-POM (i.e., before and after titration of protons by NH<sub>3</sub>), but became less sensitive to CH<sub>3</sub>OH pressure with increasing pressure (0.1–4 kPa; 453 K; Fig. 1a). ODH rates were independent of O<sub>2</sub> pressure at all O<sub>2</sub> 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<sub>3</sub>OH by lattice O-atoms (O<sup>\*</sup>) 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];

$$r_{ODH} = \frac{K_{ODH} P_{CH_3 OH}}{1 + K_{CH_3 OH} P_{CH_3 OH}}$$
(5)







**Scheme 2.** Proposed elementary steps for adsorptions of gaseous species and CH<sub>3</sub>OH dehydrogenation on lattice O-atoms (O<sup>°</sup>) in Mo-based NH<sub>4</sub>-POM clusters. Quasi-equilibrated steps are denoted by oval symbols superimposed over double arrows. Nomenclatures for reaction intermediates are shown in parentheses under each structure.

Here,  $K_{CH3OH}$  denotes the equilibrium constant for molecular adsorption of CH<sub>3</sub>OH onto O<sup>\*</sup> (step 1a; Scheme 2) and depends on the free energy of CH<sub>3</sub>OH adsorbed on O<sup>\*</sup> (CH<sub>3</sub>OH-O<sup>\*</sup>) with respect to its CH<sub>3</sub>OH(g) and O<sup>\*</sup> precursors. The  $k'_{ODH}$  (= $k_{ODH}K_{CH3OH}$ )



**Fig. 1.** CH<sub>3</sub>OH ODH rates (per POM-ks) measured from CH<sub>3</sub>OH-O<sub>2</sub> mixtures on H-POM ( $\bigstar$ ) and NH<sub>4</sub>-POM ( $\blacklozenge$ ) at 453 K as a function of (a) CH<sub>3</sub>OH pressure (0.1–4 kPa) at 20 kPa O<sub>2</sub> and (b) O<sub>2</sub> pressure (1–35 kPa) at 4 kPa CH<sub>3</sub>OH. Dashed curves represent the best regression fits to the functional form of Eq. (5).

term is the first-order rate constant for CH<sub>3</sub>OH ODH on O<sup>\*</sup> and reflects the free energy of a kinetically-relevant H-abstraction TS (step 2; Scheme 2) with respect to its CH<sub>3</sub>OH(g) and O<sup>\*</sup> precursors. The two denominator terms reflect the relative coverages of O<sup>\*</sup> and CH<sub>3</sub>OH-O<sup>\*</sup>. ODH rates become zero-order in CH<sub>3</sub>OH at high CH<sub>3</sub>OH pressures, indicative of a shift from O<sup>\*</sup> to CH<sub>3</sub>OH-O<sup>\*</sup> as the most abundant surface intermediate (MASI) with increasing CH<sub>3</sub>OH pressure. The functional form of Eq. (5) accurately describes measured CH<sub>3</sub>OH ODH rates (Fig. 1) and the regression of these data to the functional form of Eq. (5) gives the  $k'_{ODH}$  and  $K_{CH3OH}$  values on these catalysts (Table S1, SI).

Measured k'ODH values were ten-fold smaller on NH4-POM (0.5  $\pm 0.1 (kPa POM ks)^{-1}$ ) than on H-POM (5  $\pm 1 (kPa POM ks)^{-1}$ ), as a result of a decrease in the H-atom abstraction ability of lattice Oatoms  $(O^*)$  when the replacement of  $H^+$  with  $NH_4^+$  leads to a higher electron density in the oxide clusters [3]. Such H-atom abstraction ability of O<sup>\*</sup> is determined by the stability of <sup>\*</sup>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  $NH_3$  (-303 kJ mol<sup>-1</sup> on H-POM and -292 kJ mol<sup>-1</sup> on NH<sub>4</sub>-POM; Table S1, SI), consistent with Oatoms that are weaker H-abstractors in NH<sub>4</sub>-POM than in H-POM clusters and with the lower ODH turnover rates observed on NH<sub>4</sub>-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  $(O_{b1} \text{ and } O_{b2}; \text{ atom locations indicated in Fig. 2})$  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<sup>+</sup> with NH<sub>4</sub><sup>+</sup> (-303 to -292 kI mol<sup>-1</sup>) 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<sup>-1</sup> (453 K, 1 bar CH<sub>3</sub>OH; Table S1). Measured K<sub>CH30H</sub> values were similar on H and NH<sub>4</sub> forms of POM clusters  $(0.8 \pm 0.3 \text{ kPa}^{-1} \text{ and } 0.4 \pm 0.1 \text{ for H-POM and NH}_4\text{-POM, respec-}$ tively; Table S1). Their similar and near unity values are consistent with DFT-derived CH<sub>3</sub>OH adsorption free energies, which were -1 and -2 kJ mol<sup>-1</sup> on O<sub>b1</sub> in H-POM and NH<sub>4</sub>-POM, respectively (453 K, 1 bar CH<sub>3</sub>OH; Table S1).

ODH rates were not affected by  $O_2$  pressure (Fig. 1b), reflecting the prevalence of O<sup>\*</sup> species and presence of reduced centers and O<sub>2</sub>-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  $O_2$  activation pathways. Consequently, inferences about the mechanism and the identity and reactive properties of O<sub>2</sub>-derived intermediates require their reactive scavenging to form specific products during ODH reactions. Here, C<sub>3</sub>H<sub>6</sub> alkene is used as a probe molecule during CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH ODH (Sections 3.2 and 3.4) in order to detect the presence of bound O<sub>2</sub>-derived minority species formed in re-oxidation pathways without disturbing the nature or turnover rates of ODH pathways. In doing so, we demonstrate a generalized method of inquiry into the kinetically-irrelevant re-oxidation part of Mars-van Krevelen catalytic cycles by scavenging reactive O-derived species through chemical reactions that form specific detectable products. The conclusions reached are confirmed by DFT-derived free energy estimates for plausible elementary steps, which account for the identity of O<sub>2</sub>-derived species derived from scavenging reactions by C<sub>3</sub>H<sub>6</sub> and for the rate of their formation and consumption (Sections 3.3 and 3.5).



**Scheme 3.** Proposed elementary steps for the re-oxidation of reduced Mo-based NH<sub>4</sub>-POM clusters by  $O_2(g)$  and the decomposition of bound peroxo (OO<sup>\*</sup>) species and gaseous  $H_2O_2$  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  $H_2O$  from  $H/OH^*$  generates \* (step 3). Inner and outer sphere  $O_2$  activation routes on \* and  $H/OH^*$  lead to form OO<sup>\*</sup> and  $H_2O_2(g)$ , respectively (steps 4a and 4b). Reactions of OO<sup>\*</sup> with CH<sub>3</sub>OH or C<sub>3</sub>H<sub>6</sub> regenerate O<sup>\*</sup> (steps 5a and 5b).  $H_2O_2$  reacts with a reduced center (\* or  $H/OH^*$ ) to regenerate O<sup>\*</sup> and release  $H_2O$ , or with O<sup>\*</sup> to form OO<sup>\*</sup> and  $H_2O$  (steps 6a and 6b).

#### 3.2. CH<sub>3</sub>OH-O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> reactions on NH<sub>4</sub>-POM clusters

The use of NH<sub>4</sub>-POM clusters (instead of H-POM) prevents alkene oligomerization and alkanol elimination and condensation reactions that occur readily on Brønsted acids; these side reactions form oligomers that block active sites of protons (H<sup>+</sup>) and lattice O-atoms (O<sup>\*</sup>) in H-POM clusters, especially when C<sub>3</sub>H<sub>6</sub> is added to CH<sub>3</sub>OH-O<sub>2</sub> reactants (Fig. S3). In contrast with CH<sub>3</sub>OH-O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> reactions on H-POM clusters, CH<sub>3</sub>OH ODH and C<sub>3</sub>H<sub>6</sub> epoxidation on NH<sub>4</sub>-POM did not show detectable deactivation (Fig. S4). The titration of protons by NH<sub>3</sub> also inhibited C<sub>3</sub>H<sub>6</sub> hydration to 2-propanol, which can subsequently dehydrogenate on O<sup>\*</sup> sites to form acetone, a molecule that can also be formed via hydride shifts in propene oxide, the primary product in propene epoxidation.

 $C_3H_6$  epoxidation products were detected on NH<sub>4</sub>-POM only when CH<sub>3</sub>OH was also present in O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> mixtures at 453 K, indicating that lattice O-atoms (O<sup>\*</sup>) in NH<sub>4</sub>-POM clusters on their own cannot catalyze epoxidation turnovers. Epoxidation events require that CH<sub>3</sub>OH molecules dehydrogenate at O<sup>\*</sup> sites and form reduced centers, which can then react with O<sub>2</sub> to form the electrophilic dioxygen species that are required for inserting an O-atom into the C=C bonds of C<sub>3</sub>H<sub>6</sub>. Such O<sub>2</sub> activation routes have been



**Fig. 2.** DFT-derived structures for  $(NH_4)_3PMo_{12}O_{40}$  (NH<sub>4</sub>-POM) Keggin type polyoxometalate clusters. O-atoms labeled as b1 to b3 are used for probing energetics of elementary steps involved in redox cycles.

proposed to involve bound peroxo (OO<sup>\*</sup>) 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<sup>\*</sup> intermediates.

The primary epoxidation product, propene epoxide, subsequently isomerizes to acetone [32], leading to acetone to propene epoxide molar ratios that increase linearly with increasing  $C_3H_6$ conversion but extrapolate to zero values as conversion decreases (Fig. S5). Epoxidation rates ( $r_{Epox}$ ) are thus given by the combined molar formation rates of propene epoxide ( $r_{PE}$ ) and acetone ( $r_{Ace}$ ). The effects of  $C_3H_6$ ,  $H_2O$ ,  $CH_3OH$ , and  $O_2$  pressures on  $CH_3OH$ ODH and  $C_3H_6$  epoxidation rates are examined next in the context of plausible  $O_2$  activation elementary steps.

#### 3.2.1. Effect of $C_3H_6$ on $CH_3OH$ ODH and $C_3H_6$ epoxidation rates

CH<sub>3</sub>OH ODH rates were essentially unaffected by changes in C<sub>3</sub>H<sub>6</sub> pressure (0–35 kPa; 453 K; Fig. 3a), indicating that C<sub>3</sub>H<sub>6</sub>-derived bound species are present at low coverages on O<sup>\*</sup> (step 1c; Scheme 2). Thus, C<sub>3</sub>H<sub>6</sub> epoxidation rates can be used to identify the involvement of bound O<sub>2</sub>-derived intermediates during reoxidation 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<sub>3</sub>H<sub>6</sub> pressures, but increased with increasing C<sub>3</sub>H<sub>6</sub> pressure and approached a constant value above 8 kPa C<sub>3</sub>H<sub>6</sub> (Fig. 3a); this constant value corresponds to maximum epoxidation rates.

Schemes 2 and 3 show plausible routes for the reduction [3,44] and re-oxidation [11,14,21,44] of NH<sub>4</sub>-POM clusters during CH<sub>3</sub>OH ODH occurring via Mars-van Krevelen redox cycles. Re-oxidation routes also include a step accounting for the scavenging of bound O<sub>2</sub>-derived species via  $C_3H_6$  epoxidation [29,45]. In the NH<sub>4</sub>-POM reduction steps, the molecular adsorption of CH<sub>3</sub>OH on lattice O-atoms (O<sup>\*</sup>; step 1a; Scheme 2) precedes the kinetically-relevant H-abstraction step to form HCHO and a vicinal hydroxyl pair (H/OH<sup>\*</sup>; step 2; Scheme 2) [3,44]. H<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub> molecules can also adsorb and occupy active O<sup>\*</sup> 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<sub>2</sub> to regenerate the oxidized centers (O<sup>\*</sup>), 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<sub>2</sub> activation occurs via either inner and outer sphere routes to form O<sub>2</sub>-derived species with concurrent two-electron re-oxidization of reduced NH<sub>4</sub>-POM clusters (steps 4a and 4b; Scheme 3). At the other branching point, OO<sup>\*</sup> consumption can occur via parallel reactions with either CH<sub>3</sub>OH or C<sub>3</sub>H<sub>6</sub> (steps 5a and 5b; Scheme 3). The kinetic responses of epoxidation and ODH rates and their ratios to C<sub>3</sub>H<sub>6</sub> pressure are discussed in the context of the contributions of the parallel routes at these two branching points.

Inner sphere routes involve recombinative  $H_2O$  desorption from  $H/OH^*$  to form O-vacancies (\*) (step 3; Scheme 3). Subsequent  $O_2$ 



**Fig. 3.**  $C_3H_6$  epoxidation and CH<sub>3</sub>OH ODH rates (per POM-ks) measured on NH<sub>4</sub>-POM at 453 K as a function of (a)  $C_3H_6$  pressure (1–35 kPa; 1 kPa CH<sub>3</sub>OH and 20 kPa  $O_2$ ) and (b) H<sub>2</sub>O pressure (0.01–0.45 kPa; 1 kPa CH<sub>3</sub>OH, 20 kPa  $O_2$ , 35 kPa  $C_3H_6$ ). Dashed curves represent the best regression fits to the functional form of rate equations for  $C_3H_6$  epoxidation and CH<sub>3</sub>OH ODH in Scheme 4.

activation at \* forms bound peroxo (OO<sup>\*</sup>) species (step 4a; Scheme 3), which can be scavenged by  $C_3H_6$  to form epoxide with the regeneration of one O<sup>\*</sup> (step 5b; Scheme 3). The rate of epoxidation ( $r_{Epox}$ ) via OO<sup>\*</sup> species is given by:

$$r_{Epox} = k_{Epox} P_{C_3 H_6} [00^*], \tag{6}$$

where  $k_{Epox}$  denotes the first-order rate constant for C<sub>3</sub>H<sub>6</sub> epoxidation on OO<sup>\*</sup> (step 5b; Scheme 3) and depends on the free energy difference between a kinetically-relevant O-insertion TS and its C<sub>3</sub>H<sub>6</sub>(g) and OO<sup>\*</sup> precursors. When C<sub>3</sub>H<sub>6</sub> epoxidation accounts for all OO<sup>\*</sup> consumption events, the pseudo-steady-state concentration of OO<sup>\*</sup> species is given by the ratio of their formation rate ( $r_{OO^*}$ ) to  $k_{Epox}P_{C3H6}$ ;

$$[OO^*] = \frac{r_{OO^*}}{k_{Epox}P_{C_3H_6}},\tag{7}$$

which upon substitution into Eq. (6) would lead to  $r_{Epox}$  values that are independent of  $C_3H_6$  pressure and equal to  $r_{OO^*}$  at all pressures. Measured epoxidation rates, however, initially increased with increasing  $C_3H_6$  pressure before reaching a constant value (Fig. 3a). These trends are indicative of the involvement of alternate OO<sup>\*</sup> consumption routes that compete with epoxidation events and which must occur in order to complete the re-oxidation pathways in the absence of  $C_3H_6$ . DFT calculations suggest that such routes may involve OO<sup>\*</sup> decomposition via reactions with CH<sub>3</sub>OH (step 5a; Scheme3), ultimately leading to the regeneration of O<sup>\*</sup> along with a formation of HCHO and H<sub>2</sub>O (Section 3.5.1).

The initial increase in epoxidation rates with C<sub>3</sub>H<sub>6</sub> 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 C<sub>3</sub>H<sub>6</sub> to CH<sub>3</sub>OH ratio increases. The epoxidation rates become less sensitive to C<sub>3</sub>H<sub>6</sub> pressure (>8 kPa) as most of the OO<sup>\*</sup> species are scavenged by C<sub>3</sub>H<sub>6</sub> instead of CH<sub>3</sub>OH and reach asymptotic values that reflect epoxidation rates that become equal to those for OO<sup>\*</sup> formation  $(r_{00^*}, \text{Eqs. (6) and (7)})$ . The rates of NH<sub>4</sub>-POM reduction by CH<sub>3</sub>OH dehydrogenation (step 2; Scheme 2) must be equal to the reoxidation rates at steady-state: therefore, these asymptotic values would equal the CH<sub>3</sub>OH 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 ODH rates (Fig. 3a), indicative of the involvement of alternate re-oxidation routes that exclude OO<sup>\*</sup> intermediates.

Such conclusions are also evident from the ratio of the rates of epoxidation and ODH ( $r_{Epox}/r_{ODH}$ ), shown as a function of  $C_3H_6$  pressure (0–35 kPa; 453 K) in Fig. 4. The asymptotic ( $r_{Epox}/r_{ODH}$ ) ratios (for  $C_3H_6/CH_3OH > 8$ ) reflect conditions for which OO<sup>\*</sup> 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 NH<sub>4</sub>-POM clusters that must equal their re-oxidation rates at steady-state. Thus, asymptotic  $r_{Epox}/r_{ODH}$  values represent the fraction of re-oxidation events that occur through OO<sup>\*</sup> intermediates. These fractions are much smaller than unity (<0.1; Fig. 4), consistent with the prevalent involvement of re-oxidation pathways other than OO<sup>\*</sup>-mediated routes to re-oxidation rates.

These alternate re-oxidation routes may involve protoncoupled electron-transfer from vicinal OH pairs (H/OH<sup>\*</sup>) at reduced centers to gaseous or weakly-bound O<sub>2</sub>, leading to the formation of H<sub>2</sub>O<sub>2</sub> (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 H<sub>2</sub>O<sub>2</sub> formed in these two-electron re-oxidation steps can diffuse and re-oxidize another two-electron reduced center (\* or H/OH<sup>\*</sup>; step 6a; Scheme 3) [12], thus completing the four-electron re-oxidation process required



**Fig. 4.** Ratios of C<sub>3</sub>H<sub>6</sub> epoxidation and CH<sub>3</sub>OH ODH rates ( $r_{Epox}/r_{ODH}$ ) as a function of C<sub>3</sub>H<sub>6</sub> pressure ( $\checkmark$ , 1–35 kPa; 1 kPa CH<sub>3</sub>OH, 20 kPa O<sub>2</sub>) and H<sub>2</sub>O pressure ( $\diamondsuit$ , 0.01–0.45 kPa; 1 kPa CH<sub>3</sub>OH, 20 kPa O<sub>2</sub>, 35 kPa C<sub>3</sub>H<sub>6</sub>) on NH<sub>4</sub>-POM at 453 K. Dashed curves represent the best regression fits of the rate data in Fig. 3 to the functional form of rate equations for C<sub>3</sub>H<sub>6</sub> epoxidation and CH<sub>3</sub>OH ODH in Scheme 4.

for  $O_2(g)$  to act as the stoichiometric oxidant in Mars-van Krevelen cycles. The involvement of parallel inner and outer sphere  $O_2$  activation routes (steps 4a and 4b; Scheme 3) is consistent with DFTderived activation free energies, as shown by detailed assessments of energies for intermediates and transition states involved in these two  $O_2$  activation paths (Section 3.3).

#### 3.2.2. Effects of $H_2O$ on $CH_3OH$ ODH and $C_3H_6$ epoxidation rates

The re-oxidation steps in Scheme 3 include parallel inner and outer sphere O<sub>2</sub> activation routes mediated by O<sub>2</sub> reactions with either \* or H/OH<sup>\*</sup> to form OO<sup>\*</sup> or H<sub>2</sub>O<sub>2</sub>, respectively (steps 4a and 4b; Scheme 3). As a result, their relative contributions depend on the ratio of \* and H/OH<sup>\*</sup> coverages ([\*]/[H/OH<sup>\*</sup>]), which decreases with increasing H<sub>2</sub>O pressure as a consequence of the equilibration of step 3 (Scheme 3). These effects of H<sub>2</sub>O are probed here by measuring (r<sub>Epox</sub>/r<sub>ODH</sub>) ratios at different H<sub>2</sub>O pressures and high C<sub>3</sub>H<sub>6</sub>/CH<sub>3</sub>OH ratios to ensure that OO<sup>\*</sup> species exclusively react with C<sub>3</sub>H<sub>6</sub> to form epoxidation products (step 5b; Scheme 3) instead of reacting with CH<sub>3</sub>OH (step 5a; Scheme 3).

CH<sub>3</sub>OH ODH rates (without added  $C_3H_6$ ) decreased with increasing H<sub>2</sub>O pressure (Fig. S6) because of competitive adsorption of H<sub>2</sub>O with CH<sub>3</sub>OH on O<sup>\*</sup> (steps 1a and 1b; Scheme 2) [3];

$$r_{ODH} = \frac{k'_{ODH} P_{CH_3 OH}}{1 + K_{CH_3 OH} P_{CH_3 OH} + K_{H_2 O} P_{H_2 O}}$$
(8)

Here,  $K_{CH3OH}$  and  $K_{H2O}$  are the equilibrium constants for molecular adsorption of CH<sub>3</sub>OH and H<sub>2</sub>O on O<sup>\*</sup>, respectively (steps 1a and 1b; Scheme 2), and  $k'_{ODH}$  (= $K_{CH3OH}$   $k_{ODH}$ ) denotes the first-order rate constant for CH<sub>3</sub>OH ODH (step 2; Scheme 2). The functional form of Eq. (8) accurately describes all rate data (Fig. S6) with larger regressed values for  $K_{H2O}$  (8 ± 4 kPa<sup>-1</sup>) than for  $K_{CH3OH}$  (0.4 ± 01 kPa<sup>-1</sup>).

CH<sub>3</sub>OH ODH and C<sub>3</sub>H<sub>6</sub> epoxidation rates are shown in Fig. 3b as a function of H<sub>2</sub>O pressure (0.01–0.45 kPa; 453 K). Acetone can be formed via propene oxide isomerization but also via C<sub>3</sub>H<sub>6</sub> hydration when H<sub>2</sub>O is co-fed; such contributions were excluded from

 $C_3H_6$  conversion rates by subtracting acetone formation rates measured with  $O_2-C_3H_6-H_2O$  mixtures from those measured with  $CH_3-OH-O_2-C_3H_6-H_2O$  reactants (details in SI, Section S4). ODH rates decreased with increasing  $H_2O$  pressure, but epoxidation rates decreased even more strongly (Fig. 3b), as evident from ( $r_{Epox}/r_{ODH}$ ) ratios that decreased with increasing  $H_2O$  pressure (Fig. 4). These  $r_{Epox}/r_{ODH}$  ratios reflect the fraction of re-oxidation events occurring via OO<sup>\*</sup>-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  $H_2O$  concentrations increase (step 4b; Scheme 3).

The formation of C<sub>3</sub>H<sub>6</sub> epoxidation products from CH<sub>3</sub>OH-O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> reactions, but not from O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> reactions, indicates that inner sphere routes mediated by bound peroxo (OO<sup>\*</sup>) species are involved in the re-oxidation of reduced NH<sub>4</sub>-POM by O<sub>2</sub>, as also proposed in  $O_2$  activation during homogeneous oxidations [12– 14], because such O<sub>2</sub>-derived species are active for insertion of O-atoms into alkenes [46,47]. These reaction routes are also found in monooxygenase enzymes that form electrophilic peroxo (OO<sup>\*</sup>) species via O<sub>2</sub> reactions with two-electron reduced centers to perform O-insertions into C=C or C-H bonds in alkanes, alkenes and arenes [15]. These mechanisms, demonstrated here for oxidation of gaseous substrates on solid catalysts, offer strategies for using alkanols as sacrificial reductants to form bound peroxo (OO<sup>\*</sup>) species for propene epoxidation, while forming alkanals as useful coproducts. Therefore, these epoxidation routes using sacrificial reductants, after appropriate optimization, may provide alternatives to H<sub>2</sub>O<sub>2</sub> and organic peroxides as epoxidation reagents, an approach considered in homogeneous systems [46,47].

OO<sup>-</sup>-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<sub>2</sub>O was added (Fig. 4) because the conversion of reduced centers from \* to H/OH<sup>\*</sup> (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  $H_2O$  from vicinal OH groups (H/OH<sup>\*</sup>) to form O-vacancies (\*) and the subsequent irreversible  $O_2$  activation on \* to form OO<sup>\*</sup> (steps 3 and 4a; Scheme 3). Their rate ( $r_{in}$ ) is given by:

$$r_{in} = k_{in} P_{O_2}[*] = \frac{k_{in}}{K_w P_{H_2O}} P_{O_2}[H/OH^*] = \frac{k'_{in}}{P_{H_2O}} P_{O_2}[H/OH^*]$$
(9)

 $K_w$  denotes the equilibrium constant for the interconversion of H/ OH<sup>\*</sup> to form \* (step 3; Scheme 3) and k<sub>in</sub> denotes the first-order rate constant for O<sub>2</sub> activation on \* to form OO<sup>\*</sup> (step 4a; Scheme 3). The rate of outer sphere routes (r<sub>out</sub>) to form H<sub>2</sub>O<sub>2</sub>(g) via irreversible O<sub>2</sub> activation on H/OH<sup>\*</sup> species (steps 4b; Scheme 3) is given by:

$$r_{out} = k_{out} P_{O_2} [H/OH^*] \tag{10}$$

where  $k_{out}$  denotes the first-order rate constant for O<sub>2</sub> activation on H/OH<sup>\*</sup> to form H<sub>2</sub>O<sub>2</sub>(g) (step 4b; Scheme 3).

Efficient epoxidation events during CH<sub>3</sub>OH ODH turnovers require the catalytic system to preferentially re-oxidize via OO<sup>\*</sup>mediated inner sphere routes. The contributions from inner and outer sphere O<sub>2</sub> activation are given by their rate ratios ( $r_{in}/r_{out}$ , defined as  $\chi$ );

$$\chi = \frac{r_{in}}{r_{out}} = \frac{k_{in} P_{O_2}[*]}{k_{out} P_{O_2}[H/OH^*]} = \frac{k'_{in}}{k_{out} P_{H_2O}},$$
(11)

which depends on the ratio of the respective rate parameters  $(k'_{in}/k_{out})$  and on the H<sub>2</sub>O pressure. These rate parameters,  $k'_{in}$  (= $k_{in}/K_w$ ) and  $k_{out}$ , reflect in turn the free energies of formation of the transition states for inner and outer sphere O<sub>2</sub> activation routes from common O<sub>2</sub>(g) and H/OH<sup>\*</sup> 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<sub>2</sub> in its most stable triplet ground state (two unpaired p-electrons) reacts with reduced centers (\* or H/OH\*) to form O<sub>2</sub>derived species ( $OO^*$  or  $H_2O_2$ ) 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 spinunrestricted 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<sub>2</sub> activation routes on NH<sub>4</sub>-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<sup>\*</sup>) product is more stable in the singlet state. The initial O<sub>2</sub> 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<sup>\*</sup> 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<sub>in</sub>, Fig. 5), which has an electronic energy of 141 kJ mol<sup>-1</sup> before ZPVE corrections relative to O<sub>2</sub>(g) and H/OH<sup>\*</sup> precursors.

 $O_2$  reactions with transition-metals can lead to peroxo species (OO<sup>\*</sup>) 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  $\eta^1$ -superoxo intermediates, which convert to  $\eta^2$ -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<sub>4</sub>-POM clusters (Fig. 5) with TS<sub>in</sub> representing that for the first electron-transfer

Step (4a)  $O_2(g) + * \rightarrow OO^*$  (inner sphere route)

**Fig. 5.** Minimum energy path (MEP) for (a, b) inner and (c, d) outer sphere  $O_2$  activation routes (steps 4a and 4b; Scheme 3) on NH<sub>4</sub>-POM. Panels (a) and (c) show MEP curves on triplet potential energy surfaces with singlet (spin-polarized) state single-point energies of each structure shown for comparison. Panels (b) and (d) show converged singlet state (spin-polarized) MEP curves with triplet state single-point energies of structures. Transition states energies ( $\blacktriangle$ ; TS<sub>in</sub>, TS<sub>out</sub> (a) and TS<sub>out</sub> (b)) are calculated using dimer calculations started from the images at the highest MEP (TS<sub>in</sub>, TS<sub>out</sub> (a); triplet state) or at the singlet-triplet crossing point (TS<sub>out</sub> (b); spin-polarized singlet state). All energies are referenced to common  $O_2(g)$  and H/OH<sup>+</sup> precursors.

step to form  $\eta^1$ -superoxo. The O<sub>2</sub> moiety in TS<sub>in</sub> (Fig. 6f) assumes an end-on ( $\eta^1$ ) geometry with an O=O bond distance of 0.125 nm, which lies between the bond distances in O<sub>2</sub>(g) (0.123 nm) and in  $\eta^1$ -superoxo complexes of transition metals (0.128–0.130 nm) [51,52]. The O<sub>2</sub> moiety at TS<sub>in</sub> also acquires a negative charge that is much smaller than for a full electron (0.12 e<sup>-</sup>). The undercoordinated O-atom in TS<sub>in</sub> (O"-atom; Fig. 6f) reacts with the Mo center and converts to the  $\eta^2$ -peroxo products (Fig. 6 g) via a kinetically-irrelevant second electron-transfer step; no other barrier was found between TS<sub>in</sub> and  $\eta^2$ -superoxo product (Fig. 5). The bound peroxo (OO<sup>\*</sup>) product state on NH<sub>4</sub>-POM clusters has an O = O bond length (0.143 nm; Fig. 6 g) similar to that for sideon  $\eta^2$ -peroxo-Mo complexes (0.148 nm) [52] and a negative charge slightly greater than a full electron (-1.1 e<sup>-</sup>) at the O<sub>2</sub> moiety.

The MEP for outer sphere O<sub>2</sub> activation routes, involving H<sub>2</sub>O<sub>2</sub> formation via O<sub>2</sub> reactions with H/OH<sup>\*</sup> (step 4b; Scheme 3), includes a sequential transfer of two H-atoms in H/OH<sup>\*</sup> to O<sub>2</sub>(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<sub>2</sub>(g) forms a bound OOH intermediate in the triplet state via a TS (TS<sub>out</sub> (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 brokensymmetry TS (TS<sub>out</sub> (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<sub>out</sub> (a); Fig. 6i) lies at the highest energy point along the MEP with a 14 kJ mol<sup>-1</sup> barrier (electronic energy without ZPVE corrections) relative to  $O_2(g)$  and H/OH<sup>\*</sup> precursors. The TS for the second H-atom transfer (TS<sub>out</sub> (b); Fig. S10) exhibits a slightly lower barrier (9 kJ mol<sup>-1</sup>, 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<sub>4</sub>-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 endoergic with a free energy change of 59 kJ mol<sup>-1</sup> and involves a TS





**Fig. 6.** DFT-derived free energies (kJ mol<sup>-1</sup>; 453 K, 1 bar) and optimized structures of intermediates and transition states involved in O<sub>2</sub> activation on NH<sub>4</sub>-POM via inner and outer sphere routes (steps 3, 4a and 4b; Scheme 3). Gibbs free energies are referenced to the common precursors of H/OH<sup>\*</sup> and O<sub>2</sub>(g).

 $(TS_w, Fig. 6b)$  with a free energy barrier of 70 kJ mol<sup>-1</sup>. The subsequent desorption of H<sub>2</sub>O forms an O-vacancy (\*; Fig. 6d), which is slightly endoergic ( $\Delta G_{des} = 5 \text{ kJ mol}^{-1}$ ) in spite of the entropy gained upon H<sub>2</sub>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<sub>2</sub> on O-vacancies (\*) is also endoergic ( $\Delta G_{ads} = 21 \text{ kJ mol}^{-1}$ ) because of weak binding and of the loss of translational entropy upon O<sub>2</sub> binding. Bound O<sub>2</sub> species at \* (\*-O<sub>2</sub>; Fig. 6e) react via a TS (TS<sub>in</sub>; Fig. 6f) and this step has a free energy barrier of 22 kJ mol<sup>-1</sup> (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  $H_2O(g)$  from  $H/OH^*$  is quasi-equilibrated (step 3; Scheme 3). Such equilibration is consistent with the decrease in  $r_{Epox}/r_{ODH}$  ratios upon adding H<sub>2</sub>O due to a shift in the \* and H/ OH<sup>\*</sup> equilibrium towards the latter (Fig. 4).

In the outer sphere routes (step 4b; Scheme 3), O<sub>2</sub>(g) adsorbs weakly on H/OH<sup>\*</sup> ( $\Delta G_{ads} = 22$  kJ mol<sup>-1</sup>; H/OH<sup>\*</sup>-O<sub>2</sub>, Fig. 6h). Bound O<sub>2</sub> species react with surface O–H bonds to form H<sub>2</sub>O<sub>2</sub> and O<sup>\*</sup> (O<sup>\*</sup>-H<sub>2</sub>O<sub>2</sub>; Fig. 6j) via a TS (TS<sub>out</sub> Fig. 6i), and this O<sub>2</sub> activation step has a free energy barrier of 56 kJ mol<sup>-1</sup>, referenced to bound O<sub>2</sub> and H/OH<sup>\*</sup>. H<sub>2</sub>O<sub>2</sub> molecules bound on O<sup>\*</sup> desorb in an excergic step ( $\Delta G_{des} = -10$  kJ mol<sup>-1</sup>).

The kinetic relevance of inner and outer sphere  $O_2$  activation routes during re-oxidation events can be assessed by their rate ratios ( $r_{in}/r_{out}$ , defined as  $\chi$ ; Eq. (11)), which depends on the ratio of the respective rate parameters ( $k'_{in}/k_{out}$ ) and on the H<sub>2</sub>O pressure. These rate parameters,  $k'_{in}$  ( $k_{in}/K_w$ ) and  $k_{out}$ , reflect the free energies of  $O_2$  activation transition states that are referenced to the common precursors of  $O_2(g)$  and H/OH<sup>\*</sup>, as shown in Fig. 6 (107 and 78 kJ mol<sup>-1</sup> for TS<sub>in</sub> and TS<sub>out</sub>, 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 $O_2$ activation routes

DFT-derived electronic energies, enthalpies, entropies and free energies for O<sub>2</sub> activation via inner and outer sphere routes are shown in Table 1. Uncertainties in calculating low-frequency vibrational modes (less than  $\sim 150 \text{ cm}^{-1}$ ) 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  $O_2(g)$ , 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 O<sub>2</sub> 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 are also shown in Table 1 for comparison. The ratio of reoxidation rates via inner and outer sphere routes ( $\chi = r_{in}/r_{out}$ ) based on these two different sets of assumptions are shown in Fig. 7a. At a given temperature, the removal of low-frequency vibrations (the dashed line; Fig. 7a) leads to much smaller  $\chi$  values

#### Table 1

DFT-derived electronic energies ( $\Delta E^{\ddagger}$ ), enthalpies ( $\Delta H^{\ddagger}$ ), entropies ( $\Delta S^{\ddagger}$ ), and Gibbs free energies ( $\Delta G^{\ddagger}$ ) of the transition states for inner and outer sphere  $O_2$  activation routes (steps 4a and 4b; Scheme 3) referenced to common H/OH\* and O2(g) precursors on NH<sub>4</sub>-POM. DFT-derived structures of transition states are shown in Fig. 6.

	Inner sphere route (steps 4a; Scheme 3)	Outer sphere route (step 4b; Scheme 3)
$\Delta E^{\ddagger} (kJ mol^{-1})^{a}$ $\Delta H^{\ddagger} (kJ mol^{-1})^{b}$ $\Delta S^{\ddagger} (J mol^{-1} K^{-1})^{b}$	141 131 (134) 54 (9)	14 9 (10) -152 (-140)
$\Delta G^{\ddagger}$ (kJ mol <sup>-1</sup> ) <sup>D</sup>	107 (92)	78 (73)

<sup>a</sup> At 0 K in vacuum, without zero-point vibrational energy corrections.

<sup>b</sup> 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 O<sub>2</sub>(g), respectively.



than 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 ( $\chi$  =  $r_{in}/r_{out}$ ) 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 H<sub>2</sub>O, 453 K) lies within the two sets of DFT-derived values for the two different assumptions about low-frequency vibrational modes ( $0.01 < \chi < 4.4$ ; 0.01 kPa H<sub>2</sub>O; 453 K; Fig. 7a).

The  $\chi$  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 H<sub>2</sub>O pressures favor the outer sphere routes and lead to lower  $\chi$  values, because of a concomitant preference for H/OH<sup>\*</sup> over \* species, as also evident from measured r<sub>Epox</sub>/r<sub>ODH</sub> ratios that decrease with increasing H<sub>2</sub>O pressures (Fig. 4). High operating temperatures with low H<sub>2</sub>O contents favor OO<sup>\*</sup>-mediated inner sphere routes and thus lead to larger ratios of epoxidation to ODH rates. The  $\chi$  values (= $r_{in}/r_{out}$ ) 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 O<sub>2</sub> activation transition states, and their concomitant influences on rate constant ratios ( $k'_{in}/k_{out}$ ; Eq. (11)) and  $\chi$  values are the subject to on-going studies, the results of which will be published at a later time.

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

The relative contributions from inner and outer sphere O<sub>2</sub> activation routes (steps 4a and 4b; Scheme 3) do not depend on the

Fig. 7. DFT-derived  $\chi$  values ( $\chi = r_{in}/r_{out}$ ; Eq. (11)) on NH<sub>4</sub>-POM as a function reciprocal temperature at (a) 0.01 kPa H<sub>2</sub>O and (b) 0.01 to 10 kPa H<sub>2</sub>O. The dashed lines 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  $O_2(g)$  (values in Table 1). Differences between  $\chi$  values from these two treatments are shaded. The symbol ( $\blacksquare$ ) represents the measured  $\chi$  value (0.01 kPa H<sub>2</sub>O, 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  $\chi$  values less than unity.



#### CH<sub>3</sub>OH ODH rate equation

$$r_{oDH} = \frac{k_{ODH}'P_{CH_3OH} + \frac{k_{ODH\_OO*}P_{CH_3OH}}{k_{ODH\_OO*}P_{CH_3OH} + k_{Epox}P_{C_3H_6}} \left(\frac{k_{in}}{K_w P_{H_2O}} + \frac{k_{out}}{1 + \alpha(\frac{k_{ODH}'P_{CH_3OH}}{2k_{out}P_{O_2}})}\right) \frac{k_{ODH}'P_{CH_3OH}}{2k_{out}}}{1 + K_{CH_2OH}P_{CH_2OH} + K_{H_2O}P_{H_2O} + K_{C_3H_6}P_{C_3H_6}}$$

C<sub>3</sub>H<sub>6</sub> epoxidation rate equation

$$r_{Epox} = \frac{\frac{k_{Epox}P_{C_{3}H_{6}}}{k_{ODH_{OO}*}P_{CH_{3}OH} + k_{Epox}P_{C_{3}H_{6}}} \left(\frac{k_{in}}{K_{w}P_{H_{2}O}} + \frac{k_{out}}{1 + \alpha \frac{k'_{ODH}P_{CH_{3}OH}}{2k_{out}P_{O_{2}}}}\right) \frac{k'_{ODH}P_{CH_{3}OH}}{2k_{out}}$$

 $- 1 + K_{CH_3OH}P_{CH_3OH} + K_{H_2O}P_{H_2O} + K_{C_3H_6}P_{C_3H_6}$ 

### Estimated rate parameters

$K_{CH_3OH} = 0.21 \pm 0.06 \text{ kPa}^{-1}$	$k'_{ODH} = 0.39 \pm 0.05 \text{ (kPa-ks-POM)}^{-1}$
$K_{H_2O} = 4 \pm 1 \text{ kPa}^{-1}$	$k_{out} = 1.1 \pm 0.5 \text{ (kPa-ks-POM)}^{-1}$
$K_{C_3H_6} = 0.003 \ (\pm 0.004) \ \text{kPa}^{-1}$	$k_{in}' (= k_{in}/K_w) = 0.0011 \pm 0.0005 (\text{kPa-ks-POM})^{-1}$
	$\alpha = k_{6a}/k_{6b} = 3000 \pm 1000$
	$\beta = k_{Epox} / k_{ODH OO*} = 0.3 \pm 0.05$

**Scheme 4.** Rate equations for CH<sub>3</sub>OH ODH and C<sub>3</sub>H<sub>6</sub> epoxidation derived from steps proposed in Schemes 2 and 3 and rate parameters estimated from measured data on NH<sub>4</sub>-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 C<sub>3</sub>H<sub>6</sub> epoxidation and CH<sub>3</sub>OH ODH. Uncertainties reflect 95% confidence intervals.

total number of reduced centers present during steady-state ODH catalysis because both routes require one reduced center (\* or H/ OH<sup>\*</sup>) for O<sub>2</sub> activation (Eq. (11)). They depend only on the chemical state of these reduced centers, because [\*]/[H/OH<sup>\*</sup>] ratios and thus \* and H/OH<sup>\*</sup> concentrations are set by the equilibrium constant (K<sub>w</sub>; step 3; Scheme 3) and the prevalent H<sub>2</sub>O pressure. The completion of re-oxidation steps by O<sub>2</sub> during each ODH turnover, however, requires the ultimate consumption of these O<sub>2</sub>-derived species (OO<sup>\*</sup> and H<sub>2</sub>O<sub>2</sub>) in subsequent re-oxidation steps.

H<sub>2</sub>O<sub>2</sub> molecules formed via outer sphere O<sub>2</sub> activation routes (step 4b; Scheme 3) can desorb and react with another reduced (\* or H/OH<sup>\*</sup>) or oxidized (O<sup>\*</sup>) center in NH<sub>4</sub>-POM clusters. Homogeneous H<sub>2</sub>O<sub>2</sub> decomposition rates are undetectable below 723 K [53] and thus do not contribute at the conditions used in this study.  $H_2O_2$  can react with either type of reduced centers (\* or  $H/OH^*$ ) in  $NH_4$ -POM to form  $H_2O$  (one or two molecules from \* or H/OH<sup>\*</sup>, respectively) and re-oxidize these centers by forming O<sup>\*</sup> species (step 6a; Scheme 3) [12]. The sequential re-oxidation events via steps 4b and 6a in Scheme 3 complete the four-electron oxidation by O<sub>2</sub>, using H<sub>2</sub>O<sub>2</sub> as the molecular shuttle for the second O-atom in O<sub>2</sub>. These routes circumvent epoxidation reactions by preventing the formation of electrophilic bound OO<sup>\*</sup> species and represent the predominant re-oxidation route, as evident from epoxidation to ODH rate ratios  $(r_{epox}/r_{ODH})$  that remain much smaller than unity even at high C<sub>3</sub>H<sub>6</sub>/CH<sub>3</sub>OH ratios (Fig. 4). In contrast, H<sub>2</sub>O<sub>2</sub> reactions with oxidized centers  $(0^*)$  can form  $00^*$  and  $H_20$  (step 6b; Scheme 3), as proposed for alkene epoxidation with  $H_2O_2$  on POM clusters [29,45-47]. This  $H_2O_2$  consumption route leads to a kinetic "crossing point" between otherwise parallel outer and inner sphere O<sub>2</sub> activation routes (steps 4a and 4b; Scheme 3), because  $H_2O_2$  formed in outer sphere route forms the same  $OO^*$ species derived from inner sphere routes.

 $H_2O_2$  consumption via reactions with reduced or oxidized centers (steps 6a and 6b; Scheme 3) influences  $r_{Epox}/r_{ODH}$  ratios because reactions with reduced centers avoid the formation of OO<sup>\*</sup> and thus epoxidation. The ratio of the rates of these two  $H_2O_2$  reactions ( $r_{6a}/r_{6b}$ , defined as  $\gamma$ ) is given by:

$$\gamma = \frac{r_{6a}}{r_{6b}} = \frac{k_{6a\_*}P_{H_2O_2}[*] + k_{6a\_H/OH^*}P_{H_2O_2}[H/OH^*]}{k_{6b}P_{H_2O_2}[O^*]}$$
$$= \frac{\left(\frac{k_{6a\_*}}{K_wP_{H_2O}} + k_{6a\_H/OH^*}\right)}{k_{6b}} \frac{[H/OH^*]}{[O^*]} = \alpha \frac{[H/OH^*]}{[O^*]}$$
(12)

 $k_{6a\_*}$ ,  $k_{6a\_H/OH^*}$  and  $k_{6b}$  represent the first-order rate constants for  $H_2O_2$  reactions with \*,  $H/OH^*$  and O<sup>\*</sup> species, respectively (steps 6a and 6b; Scheme 3). The rate ratios,  $\gamma$  (=  $r_{6a}/r_{6b}$ ), depend on the value of  $\alpha$  (=( $k_{6a\_*}/K_wP_{H2O} + k_{6a\_H/OH^*}$ )/ $k_{6b}$ ) and on [ $H/OH^*$ ]/[O<sup>\*</sup>] ratios. When the contributions by OO<sup>\*</sup>-mediated routes to re-oxidation events are minor, [ $H/OH^*$ ]/[O<sup>\*</sup>] ratios are given by (detailed derivation in Section S10):

$$\frac{[H/OH^*]}{[O^*]} = \frac{k'_{ODH}P_{alkanol}}{2k_{out}P_{O_2}},$$
(13)

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  $O_2$ . The  $k'_{ODH}$  values depend on the free energy of a kinetically-relevant H-abstraction TS respect to its gaseous alkanol and  $O^*$  precursors. The substitution of Eq. (13) into Eq. (12) gives a value for  $\gamma$  (= $r_{6a}/r_{6b}$ ):

$$\gamma = \frac{r_{6a}}{r_{6b}} = \frac{\alpha k'_{ODH} P_{alkanol}}{2k_{out} P_{O_2}} \tag{14}$$

Next, we vary these  $\gamma$  values by using more reactive alkanols (C<sub>2</sub>H<sub>5</sub>OH; larger  $k'_{ODH}$  value) and different CH<sub>3</sub>OH/O<sub>2</sub> reactant ratios.

3.4.1. Effects of alkanol reactivity on ODH and C<sub>3</sub>H<sub>6</sub> epoxidation rates

Alkanol ODH and  $C_3H_6$  epoxidation rates, measured with two different alkanols ( $C_2H_5OH$  and  $CH_3OH$ ), are shown in Fig. 8a at different  $C_3H_6$  pressures (1–35 kPa; 453 K).  $C_2H_5OH$  ODH rates were about three-fold larger than for CH<sub>3</sub>OH, as expected from the weaker C—H bonds in  $C_2H_5OH$  [10,54]. Epoxidation rates approached constant asymptotic values with increasing  $C_3H_6$  pressure for both alkanols, but these values were larger for  $C_2H_5OH$ than CH<sub>3</sub>OH. These trends reflect higher OO<sup>\*</sup> formation rates



**Fig. 8.** (a) Measured rates (per POM-ks) of CH<sub>3</sub>OH ( $\blacktriangle$ ) and C<sub>2</sub>H<sub>5</sub>OH ( $\bigtriangledown$ ) ODH and C<sub>3</sub>H<sub>6</sub> epoxidation ( $\blacklozenge$  and  $\blacksquare$ , measured with CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH, respectively) and (b) the ratio of epoxidation to ODH rates for CH<sub>3</sub>OH ( $\blacklozenge$ ) or C<sub>2</sub>H<sub>5</sub>OH ( $\backsim$ ) reactants as a function of C<sub>3</sub>H<sub>6</sub> pressure (1–35 kPa) on NH<sub>4</sub>-POM at 453 K (1 kPa alkanol, 20 kPa O<sub>2</sub>). Dashed curves represent regression of the rate data to the functional form of rate equations in Scheme 4. Differences between the measurements with CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH are shaded.



**Fig. 9.** C<sub>3</sub>H<sub>6</sub> epoxidation and CH<sub>3</sub>OH ODH rates (per POM-ks) measured on NH<sub>4</sub>-POM at 453 K as a function of (a) CH<sub>3</sub>OH pressure (0.1–4 kPa; 20 kPa O<sub>2</sub>, 35 kPa C<sub>3</sub>H<sub>6</sub>) and (b) O<sub>2</sub> pressure (1–25 kPa; 1 kPa CH<sub>3</sub>OH, 35 kPa C<sub>3</sub>H<sub>6</sub>). Dashed curves represent best regression fits of the rate data to the functional form of rate equations in Scheme 4.

resulting from a higher concentration of reduced centers (\* and H/ OH<sup>\*</sup>) for the alkanol with larger ODH rate constant ( $k'_{ODH}$ ; Eq. (13)). Asymptotic epoxidation rates are much smaller than ODH rates for both alkanols, indicating that re-oxidation routes that exclude OO<sup>\*</sup> intermediates remain the predominant re-oxidation path for both reactants.

These asymptotic  $r_{Epox}/r_{ODH}$  ratios reflect the fraction of reoxidation events mediated by OO<sup>\*</sup> intermediates, either via inner sphere O<sub>2</sub> activation or via H<sub>2</sub>O<sub>2</sub> (formed in outer sphere routes) reactions with O<sup>\*</sup>. C<sub>2</sub>H<sub>5</sub>OH reductants, which lead to larger coverages of reduced centers than CH<sub>3</sub>OH, led to smaller  $r_{Epox}/r_{ODH}$  ratios and to the less prevalent involvement of OO<sup>\*</sup>-mediated routes (Fig. 8b). These data indicate that more abundant reduced centers (\* or H/OH<sup>\*</sup>) lead to a higher probability of H<sub>2</sub>O<sub>2</sub> reactions with such centers, thus forming O<sup>\*</sup>, instead of reacting with O<sup>\*</sup> to form OO<sup>\*</sup> (steps 6a and 6b; Scheme 3), leading to the higher  $\gamma$  values observed for the more reactive alkanol (Eq. (14)).

# 3.4.2. Effects of CH<sub>3</sub>OH and $O_2$ pressures on CH<sub>3</sub>OH ODH and $C_3H_6$ epoxidation rates

Both CH<sub>3</sub>OH ODH and C<sub>3</sub>H<sub>6</sub> epoxidation rates increased with increasing CH<sub>3</sub>OH pressure (<1 kPa; Fig. 9a), because reduced centers formed via CH<sub>3</sub>OH dehydrogenation (step 2; Scheme 2) act as intermediates for epoxidation events by activating O<sub>2</sub> as OO<sup>\*</sup> species. The ( $r_{Epox}/r_{ODH}$ ) ratios decreased with increasing CH<sub>3</sub>OH pressure (Fig. 10), indicating that OO<sup>\*</sup>-mediated re-oxidation routes become less prevalent as the concentration of reduced centers (\* or H/OH<sup>\*</sup>) increases. As in the case of the



**Fig. 10.** Ratios of epoxidation to ODH rates  $(r_{Epox}/r_{ODH})$  as a function of CH<sub>3</sub>OH pressure ( $\bullet$ , 0.1–4 kPa, 20 kPa O<sub>2</sub>, 35 kPa C<sub>3</sub>H<sub>6</sub>) and the reciprocal of O<sub>2</sub> pressure ( $\blacktriangle$ , 1–25 kPa, 1 kPa CH<sub>3</sub>OH, 35 kPa C<sub>3</sub>H<sub>6</sub>) on NH<sub>4</sub>-POM at 453 K. Dashed curves represent best regression fits of the rate data to the functional form of rate equations in Scheme 4.

more reactive alkanol, this reflects  $H_2O_2$  reactions with reduced centers (\* or  $H/OH^*$ ), which circumvent  $OO^*$  formation via  $H_2O_2$  reactions with  $O^*$ .

The number of reduced centers also increases as the  $O_2$  pressure decreases (Eq. (13)). Epoxidation rates increased slightly with  $O_2$  pressure, even though ODH rates remained unchanged (Fig. 9b). These trends are evident in ( $r_{Epox}/r_{ODH}$ ) ratios that decreased monotonically with the reciprocal of  $O_2$  pressures (Fig. 10), indicative of a concomitant increase in  $\gamma$  values (Eq. (14)).

The effects of alkanol reactivity and CH<sub>3</sub>OH/O<sub>2</sub> ratios on (r<sub>Epox</sub>/ r<sub>ODH</sub>) values indicate that H<sub>2</sub>O<sub>2</sub> formed via outer sphere O<sub>2</sub> 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  $H_2O_2(g)$ , which allows the second twoelectron oxidation to occur at reduced or oxidized centers present beyond molecular distances. In contrast, bound peroxo (OO<sup>\*</sup>) species can access non-vicinal reduced centers only via the activated migration of one of its O-atoms throughout oxide surfaces; such OO<sup>\*</sup> hopping routes, however, impose significant kinetic hurdles. As a result, they cannot account for the fast nature of reoxidation routes during ODH turnovers. OO<sup>\*</sup> species can decompose instead by two-electron oxidation of a gaseous reductant, either an alkanol (step 5a; Scheme 3) or an alkene (step 5b; Scheme3), thus completing the four-electron oxidation by  $O_2$ . In what follows, theoretical treatments are used to examine the routes by which  $O_2$ -derived species ( $OO^*$  or  $H_2O_2$ ) 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  $O_2$ -derived species

### 3.5.1. Decomposition routes of bound peroxo (OO<sup>\*</sup>) 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 O<sub>2</sub> 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<sup>-1</sup>) of the H-POM cluster with vicinal O-vacancies than with isolated O-vacancies (located at  $O_{b2}$  and  $O_{b3}$  versus Ob2 and Ob4; Fig. S11). This is also evident from DFT-derived HAE values, which become much less negative (by  $\sim$ 50–70 kJ mol<sup>-1</sup>) for O-atoms near a reduced center (H/OH<sup>\*</sup>) than for distant Oatoms, indicative of the unlikely formation of proximal reduced centers (Fig. S11). The decomposition of bound peroxo  $(OO^*)$  species via reactions with another reduced center  $(00^* + * \rightarrow 20^*)[11,20]$  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<sup>\*</sup> and non-vicinal H/OH<sup>\*</sup>, which represent the "reactants" in such migration events.

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

DFT-derived activation barriers for OO<sup>\*</sup> hopping steps ( $\Delta G^{\ddagger}$  = 151 kJ mol<sup>-1</sup>) are much higher than OO<sup>\*</sup> formation steps via inner or outer sphere O<sub>2</sub> activation routes (steps 3, 4a and 4b; Scheme 3; 107 and 78 kJ mol<sup>-1</sup>; Section 3.3.2). These barriers are also higher than the kinetically-relevant H-abstraction step (step 2; Scheme 2; 139 kJ mol<sup>-1</sup>) 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<sup>\*</sup> 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<sup>\*</sup> reactions with alkanols. The dearth of vicinal reduced centers and the high OO<sup>\*</sup> hopping barriers indicate that more facile OO<sup>\*</sup> decomposition routes must be involved. OO<sup>\*</sup> can react with reactant alkanols to form alkanals and H<sub>2</sub>O, regenerating O<sup>\*</sup> (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<sub>3</sub>OH adsorbs weakly on OO<sup>\*</sup> ( $\Delta$ G = 4 kJ mol<sup>-1</sup>; Fig. 12a) and reacts via a C–H activation TS (TS<sub>ODH\_OO</sub>\*; Fig. 12b) with a free energy of 94 kJ mol<sup>-1</sup>, referenced to its CH<sub>3</sub>OH(g) and OO<sup>\*</sup> precursors. This C–H activation can lead to OOH\* and a bound CH<sub>2</sub>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<sup>‡</sup> = 14 kJ mol<sup>-1</sup>, referenced to CH<sub>3</sub>OH(g) and OO\*; Fig. S12) is much lower than the C–H activation TS. The OOH\* species and vicinal OH\* formed react to release H<sub>2</sub>O and re-form O\* via a dehydration TS (TS<sub>Dehyd</sub>; 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<sub>3</sub>OH to form methane diol (Fig. 12e), which dehydrates to form HCHO and H<sub>2</sub>O via a Hatom transfer TS (TS'<sub>Dehyd</sub>; Fig. 12f) with a free energy much lower



**Fig. 11.** DFT-derived free energies (kJ mol<sup>-1</sup>; 453 K, 1 bar) and structures of intermediates and transition states involved in OO<sup>\*</sup> decomposition routes on NH<sub>4</sub>-POM via O-atom migration and reaction with another reduced center. Free energies of OO<sup>\*</sup> and H/OH<sup>\*</sup> are taken as reference.



**Fig. 12.** DFT-derived free energies (kJ mol<sup>-1</sup>; 453 K, 1 bar) and structures of intermediates and transition states on NH<sub>4</sub>-POM involved in OO<sup>\*</sup> reactions with CH<sub>3</sub>OH(g) to form O<sup>\*</sup>, HCHO(g) and H<sub>2</sub>O(g) (step 5a; Scheme 3). Two plausible reaction routes, one involving sequential C—H and O—H activations and another inserting O-atom into C—H bond are considered. Free energies of OO<sup>\*</sup> and CH<sub>3</sub>OH(g) are taken as reference.

than the C—H activation TS. In both cases, OO<sup> $\circ$ </sup> decomposes to reform O<sup> $\circ$ </sup> by reacting with CH<sub>3</sub>OH(g), ultimately leading to form HCHO and H<sub>2</sub>O.

The ratio of the rates for OO<sup>\*</sup> decomposition via oxidation of non-vicinal reduced centers (\*) to that for its oxidation of CH<sub>3</sub>OH (g) reactants ( $\delta = r_{*\_OO^*}/r_{ODH\_OO^*}$ ) is given by:

$$\delta = \frac{r_{*\_O0^{*}}}{r_{ODH\_O0^{*}}} = \frac{(k_{*\_O0^{*}} / (K_{w} P_{H_2O})[OO^{*}][H/OH^{*}]}{k_{ODH\_O0^{*}}[OO^{*}]P_{CH_3OH}}$$
(15)

Here,  $k_{ODH_OO^*}$  reflects the first-order rate constant for OO<sup>\*</sup> reaction with CH<sub>3</sub>OH(g) and depends on the free energy of a C–H activation TS (TS<sub>ODH\_OO\*</sub>; Fig. 12b), relative to its CH<sub>3</sub>OH(g) and OO<sup>\*</sup> precursors.  $K_{*,OO^*}/Kw$  denotes the rate parameter for OO<sup>\*</sup> reaction with a non-vicinal reduced center (H/OH<sup>\*</sup>) and depends on the free energy of a OO<sup>\*</sup> hopping TS (TS<sub>O\_hopping</sub>; Fig. 11a), relative to OO<sup>\*</sup> and a non-vicinal H/OH<sup>\*</sup>. The ( $k_{*,OO^*}/(K_w k_{ODH_OO^*})$ ) value calculated from DFT-derived free energies is  $3 \times 10^{-7}$  (453 K; 1 bar), which, taken together with the presence of reduced centers as minority intermediate species, indicates that  $\delta$  values are much less than unity and that CH<sub>3</sub>OH reactions with OO<sup>\*</sup> are much faster than OO<sup>\*</sup> hopping routes.

3.5.1.3.  $OO^*$  reactions with alkenes.  $C_3H_6$  molecules introduced in  $CH_3OH-O_2$  streams can also react with  $OO^*$  to form propene oxides (step 5b; Scheme 3), as shown by their formation from such reactant mixtures (Figs. 3 and 9). Fig. 13 shows DFT-derived free energies (453 K; 1 bar) and structures for the intermediates and transition states involved in  $OO^*-C_3H_6$  reactions.  $C_3H_6$  adsorbs weakly on  $OO^*$  with a reaction free energy of 22 kJ mol<sup>-1</sup> (Fig. 13a) and forms propene oxide via an O-insertion transition state (TS<sub>Epox</sub>; Fig. 13b) with an activation free energy of 103 kJ mol<sup>-1</sup>, referenced to its  $OO^*$  and  $C_3H_6(g)$  precursors.

The effects of  $C_3H_6$  pressure on epoxidation rates (<8 kPa  $C_3H_6$ ; Fig. 3a) reflect competitive CH<sub>3</sub>OH and  $C_3H_6$  reactions with OO<sup>\*</sup> (steps 5a and 5b; Scheme 3) as discussed in Section 3.2.1. The ratio of these two OO<sup>\*</sup> decomposition rates ( $\varepsilon = r_{Eoox}/r_{ODH OO^*}$ ) is:

$$\varepsilon = \frac{r_{Epox}}{r_{oDH_{-}OO^{*}}} = \frac{k_{Epox}[OO^{*}]P_{C_{3}H_{6}}}{k_{oDH_{-}OO^{*}}[OO^{*}]P_{CH_{3}OH}} = \beta \frac{P_{C_{3}H_{6}}}{P_{CH_{3}OH}}$$
(16)

Here,  $k_{ODH_OO^*}$  is the first-order rate constant for OO<sup>\*</sup> reaction with CH<sub>3</sub>OH(g) (step 5a; Scheme 3) and depends on the free energy of the C—H activation TS (TS<sub>ODH\_OO</sub>•; Fig. 12b), relative to its CH<sub>3</sub>OH (g) and OO<sup>\*</sup> precursors. The  $k_{Epox}$  term denotes the first-order rate constant for the reaction of OO<sup>\*</sup> with C<sub>3</sub>H<sub>6</sub>(g) (step 5b; Scheme 3), which reflects the free energy of an O-insertion TS (TS<sub>D\_Epox</sub>; Fig. 13b), referenced to C<sub>3</sub>H<sub>6</sub>(g) and OO<sup>\*</sup>. The value of  $\beta$  (= $k_{Epox}/k_{ODH_OO^*}$ ) derived from DFT calculations (0.12) is smaller than unity, indicating that equimolar C<sub>3</sub>H<sub>6</sub>-CH<sub>3</sub>OH reactants would preferentially decompose OO<sup>\*</sup> via reactions with CH<sub>3</sub>OH instead of C<sub>3</sub>H<sub>6</sub>. Such conclusions are consistent with epoxidation rates that increase with increasing C<sub>3</sub>H<sub>6</sub> pressure and reach constant values only for C<sub>3</sub>H<sub>8</sub>/CH<sub>3</sub>OH ratios much larger than unity (Fig. 3a).

These OO<sup>\*</sup>-mediated routes account for only a small fraction (<0.1) of all re-oxidation events during CH<sub>3</sub>OH ODH on NH<sub>4</sub>-POM clusters, as shown by asymptotic ( $r_{Epox}/r_{ODH}$ ) ratios much smaller than unity (<0.1; Fig. 4). The alternate and predominant routes mediated by H<sub>2</sub>O<sub>2</sub> molecules are discussed next.

#### 3.5.2. H<sub>2</sub>O<sub>2</sub> decomposition routes

3.5.2.1.  $H_2O_2$  reactions with reduced centers.  $H_2O_2$  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  $H_2O_2$  decomposition on \* or  $H/OH^*$ . Free energies in both cases are referenced to  $H_2O_2(g)$  and  $H/OH^*$  species to allow a rigorous comparison based on their rate ratios.

 $H_2O_2$  decomposition on O-vacancies (\*) involves molecular adsorption of  $H_2O_2$  ( $\Delta G_{ads} = -3$  kJ/mol; \*\_ $H_2O_2$ ; Fig. 14a) and reactions with a vicinal O\* via a H-transfer TS ( $\Delta G^{\ddagger} = 70$  kJ mol<sup>-1</sup>, referenced to  $H_2O_2(g)$  and H/OH\*; TS<sub>6a</sub>; Fig. 14b) to form vicinal OOH\* and OH\* (OOH/H\*; Fig. 14c). These two species then recombine to form  $H_2O(g)$  and O\* via a  $H_2O$  elimination TS (TS<sub>Dehyd</sub>; Fig. 14d) with a free energy much less than TS<sub>6a</sub>.

The decomposition of  $H_2O_2$  on  $H/OH^*$  without intervening vacancy formation involves weak  $H_2O_2$  adsorption ( $\Delta G_{ads} = 35 \text{ kJ} \text{ mol}^{-1}$ ;  $H/OH^*_-H_2O_2$ ; Fig. 14e) and a TS ( $\Delta G^\ddagger = 84 \text{ kJ mol}^{-1}$ , referenced to  $H_2O_2(g)$  and  $H/OH^*$ ;  $TS'_{6a}$ ; Fig. 14f) that leads to form two adsorbed  $H_2O$  molecules at vicinal O<sup>\*</sup> species (O<sup>\*</sup>\_2H\_2O; 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<sup>-1</sup>; 453 K, 1 bar) and structures of intermediates and transition states on NH<sub>4</sub>-POM involved in OO<sup>\*</sup> reactions with  $C_3H_6$  to form O<sup>\*</sup> and propene oxide (step 5b; Scheme 3). Free energies of OO<sup>\*</sup> and  $C_3H_6(g)$  are taken as reference.



**Fig. 14.** DFT-derived free energies (kJ mol<sup>-1</sup>; 453 K, 1 bar) and structures of intermediates and transition states on NH<sub>4</sub>-POM involved in  $H_2O_2$  reactions with a reduced center (\* or H/OH\*) to form O\* and  $H_2O$  (step 6a; Scheme 3). The panel (a) involves the reaction with \* (blue dash lines), while the panel (b) shows the reaction with H/OH \* (black solid lines). Free energies are referenced to the common  $H_2O_2(g)$  and H/OH\* precursors.

The relative rates for  $H_2O_2$  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  $H_2O$  pressure.  $H_2O_2$  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  $H_2O_2$  decomposition routes are shown together as step 6a in Scheme 3.

3.5.2.2.  $H_2O_2$  reactions with O<sup>\*</sup> 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  $H_2O_2$  reactions with O<sup>\*</sup> to form OO<sup>\*</sup> and  $H_2O$  (step 6b; Scheme 3) are shown in Fig. 15. Weakly-adsorbed  $H_2O_2$  on O<sup>\*</sup> ( $\Delta G_{ads} = 10 \text{ kJ} \text{ mol}^{-1}$ ; O<sup>\*</sup>- $H_2O_2$ ; Fig. 15a) forms vicinal hydroperoxo (O-OOH) and OH<sup>\*</sup> (denoted as O-OOH/H<sup>\*</sup>; Fig. 15c) species in a step mediated by a TS in which one H-atom is abstracted from  $H_2O_2$  by O<sup>\*</sup> (TS<sub>6b\_1</sub>; Fig. 15b). The free energy barrier is 140 kJ mol<sup>-1</sup> when referenced to  $H_2O_2(g)$  and O<sup>\*</sup>. These O-OOH/H<sup>\*</sup> species form bound peroxo species (OO<sup>\*</sup>) and  $H_2O$  via an O-insertion TS (TS<sub>6b\_2</sub>; Fig. 15d) with a free energy barrier of 158 kJ mol<sup>-1</sup> (referenced to  $H_2O_2(g)$  and O<sup>\*</sup>), 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<sup>\*</sup> species, typically associated with inner sphere routes (step 4a; Scheme 3), using the reaction of H<sub>2</sub>O<sub>2</sub>, formed in outer sphere routes (step 4b; Scheme 3), with O<sup>\*</sup> (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<sub>2</sub>O<sub>2</sub> preferentially react with O<sup>\*</sup> to form OO<sup>\*</sup> 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<sup>\*</sup>-mediated routes to re-oxidation events at typical ODH conditions. This suggests, in turn, that the H<sub>2</sub>O<sub>2</sub> molecules formed in the predominant O<sub>2</sub> activation route (step 4a; Scheme 3) react predominantly with reduced centers (\* or H/OH<sup>\*</sup>) instead of with O<sup>\*</sup>, 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<sub>2</sub>O<sub>2</sub> reactions with O<sup>\*</sup> to form OO<sup>\*</sup> (156 kJ mol<sup>-1</sup>) are much higher than for H<sub>2</sub>O<sub>2</sub> reactions with \* (70 kJ mol<sup>-1</sup>) or H/OH<sup>\*</sup> (84 kJ mol<sup>-1</sup>) to form O<sup>\*</sup> and H<sub>2</sub>O, when referenced to the same H<sub>2</sub>O<sub>2</sub>(g) precursor and to the respective surface species (O<sup>\*</sup> or H/OH<sup>\*</sup>).

The OO<sup>\*</sup> 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  $H_2O_2$  reactions with O<sup>\*</sup> (steps 4b and



**Fig. 15.** DFT-derived free energies (kJ mol<sup>-1</sup>; 453 K, 1 bar) and structures of intermediates and transition states on NH<sub>4</sub>-POM involved in H<sub>2</sub>O<sub>2</sub> reactions with an oxidized center (O) to form OO and H<sub>2</sub>O(g) (step 6b; Scheme 3). Free energies of H<sub>2</sub>O<sub>2</sub>(g) and O are taken as reference.

6b; Scheme 3). A preference for OO<sup>\*</sup>-mediated re-oxidation routes is required for high epoxidation selectivities during ODH reactions, which can be achieved by increasing  $r_{in}/r_{out}$  ratios ( $\chi$ ; Eq. (11)) and decreasing  $r_{6a}/r_{6b}$  ratios ( $\gamma$ ; Eq. (14)). An increase in  $r_{in}/r_{out}$  ratios ( $\chi$ ; Eq. (11)) leads to a larger fraction of reduced centers forming to OO<sup>\*</sup> species (instead of H<sub>2</sub>O<sub>2</sub>(g)) and can be achieved by operating at higher temperatures or lower H<sub>2</sub>O contents (Section 3.3.3). A decrease in  $r_{6a}/r_{6b}$  ratios ( $\gamma$ ; Eq. (14)) also leads to a greater preference for OO<sup>\*</sup>-mediated routes by increasing the fraction of H<sub>2</sub>O<sub>2</sub> molecules reacting with O<sup>\*</sup> to form OO<sup>\*</sup> species (and H<sub>2</sub>O) instead of with reduced centers to form O<sup>\*</sup> (and H<sub>2</sub>O). Lower \* and H/OH<sup>\*</sup> coverages minimize H<sub>2</sub>O<sub>2</sub> decomposition on such centers and lead to the higher ( $r_{6a}/r_{6b}$ ) ratios observed for less reactive alkanols and or at lower CH<sub>3</sub>OH/O<sub>2</sub> ratios (Eq. (14)).

#### 3.6. Kinetic rate equations for $CH_3OH$ ODH and $C_3H_6$ epoxidation

Schemes 2 and 3 summarize plausible routes for the reduction and re-oxidation parts of ODH cycles and for the scavenging reactions of OO<sup>\*</sup> intermediates via  $C_3H_6$  epoxidation. The rate equations for CH<sub>3</sub>OH ODH and  $C_3H_6$  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<sub>3</sub>OH ODH and  $C_3H_6$  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:

$$r_{\text{ODH}} = k'_{\text{ODH}} P_{\text{CH}_3\text{OH}}[O^*] + k_{\text{ODH}_{-}\text{OO}*} P_{\text{CH}_3\text{OH}}[OO^*]$$
(17)

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

$$[OO^*] = \frac{\left(\frac{k_{in}}{K_w P_{H_2O}} + \frac{k_{out}}{1 + \alpha \frac{k'_{ODH} P_{CH_3OH}}{2k_{out} P_{O_2}}}\right) \frac{k'_{ODH} P_{CH_3OH}}{2k_{out}}}{k_{ODH\_OO^*} P_{CH_3OH} + k_{Epox} P_{C_3H_6}} [O^*],$$
(18)

for the case of re-oxidation predominantly mediated via steps 4b and 6a (Scheme 3), as is evident from the small asymptotic  $r_{Fnox}$ /

 $r_{ODH}$  values at high  $C_3H_8/CH_3OH$  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 route (steps 4a and 4b; Scheme 3). The ratio of rate constants for  $H_2O_2$  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  $[O^*]$ :

$$[O^*] = \frac{1}{1 + K_{CH_3OH} P_{CH_3OH} + K_{H_2O} P_{H_2O} + K_{C_3H_6} P_{C_3H_6}}$$
(19)

The denominator terms reflect the relative surface concentrations of (O<sup>\*</sup>), (CH<sub>3</sub>OH-O<sup>\*</sup>), (H<sub>2</sub>O-O<sup>\*</sup>), (C<sub>3</sub>H<sub>6</sub>-O<sup>\*</sup>), 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<sub>3</sub>OH ODH and C<sub>3</sub>H<sub>6</sub> 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<sub>3</sub>H<sub>6</sub> co-reactants, the CH<sub>3</sub>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

 $C_3H_6$  molecules are used to scavenge bound  $O_2$ -derived species formed during the re-oxidation part of Mars-van Krevelen catalytic cycles for alkanol ODH on solid oxides. The effects of  $C_3H_6$ ,  $H_2O$ ,  $CH_3OH$ , and  $O_2$  pressures and the reactivity of alkanols on alkanol ODH and  $C_3H_6$  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.

 $C_3H_6$  epoxidation products are detected in  $O_2-C_3H_6$  mixtures only when alkanols are also present in reactant streams and they undergo ODH reactions. Such coupling of ODH and epoxidation reactions suggests that reduced centers formed via alkanol 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  $O_2$  activation routes mediated by bound peroxo (OO<sup>\*</sup>) species, which are ubiquitous in homogeneous POM catalysis, electro-catalysis and bio-catalysis with monooxygenase enzymes. The contributions of these OO<sup>\*</sup>-mediated routes to re-oxidation events, however, are minor for Mo-based NH<sub>4</sub>-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  $(H/OH^{*})$  to  $O_2$  to form  $H_2O_2$ , which can easily desorb and re-oxidize another reduced center (\* or  $H/OH^{*}$ ) to form  $O^{*}$  (and  $H_2O$ ). The  $H_2O_2$  molecules can also react with an oxidized center  $(O^{*})$  to form  $OO^{*}$  species (and  $H_2O$ ), creating a kinetic shunt between inner and outer sphere  $O_2$  activation routes; this shunt leads to higher epoxidation to ODH rate ratios at lower reduced center concentrations.

Unlike  $H_2O_2$  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<sup>\*</sup> species with non-vicinal reduced centers require kinetically demanding O-hopping steps that must occur several times to reach an O<sup>\*</sup> center vicinal to the reduced center. OO<sup>\*</sup> species instead can react with a gas-phase reactant, alkanol (CH<sub>3</sub>OH) and alkene (C<sub>3</sub>H<sub>6</sub>), to ultimately re-form O<sup>\*</sup> 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 reoxidation routes that prefer molecular donor ( $H_2O_2$ ) or acceptor ( $CH_3OH$  and  $C_3H_6$ ) to perform sequential two-electron oxidation events occurring at distant locations, instead of the kineticallydemanding 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  $O_2$  molecule. Such routes, upon further optimization, may provide an economic process to perform epoxidation without requiring expensive oxidants, such as  $H_2O_2$  and organic peroxides.

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#### **Appendix A. Supplementary material**

Reaction networks of alkanol-O<sub>2</sub> reactions on bifunctional catalysts; effects of NH<sub>3</sub> titrations of acid sites on CH<sub>3</sub>OH dehydration and ODH rates; time-on-stream CH<sub>3</sub>OH dehydration and ODH rates before and after introduction of C<sub>3</sub>H<sub>6</sub> co-feed on H-POM; time-on-stream CH<sub>3</sub>OH ODH, and C<sub>3</sub>H<sub>6</sub> epoxidation rates on NH<sub>4</sub>-POM; CH<sub>3</sub>OH ODH product selectivities on NH<sub>4</sub>-POM as a function of

CH<sub>3</sub>OH conversions; the values of rate and equilibrium constants for CH<sub>3</sub>OH ODH, DFT-derived reactivity-averaged HAE, Habstraction free energy barriers and CH<sub>3</sub>OH adsorption free energy changes on H-POM and NH<sub>4</sub>-POM; product selectivities of C<sub>3</sub>H<sub>6</sub> conversions during CH<sub>3</sub>OH-O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub> reactions as a function of C<sub>3</sub>H<sub>6</sub> conversions; effects of H<sub>2</sub>O on CH<sub>3</sub>OH ODH rates; acetone formation rates from O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub>-H<sub>2</sub>O reactions on NH<sub>4</sub>-POM; C<sub>3</sub>H<sub>6</sub> conversion and epoxidation rates from CH<sub>3</sub>OH-O<sub>2</sub>-C<sub>3</sub>H<sub>6</sub>-H<sub>2</sub>O reactions on NH<sub>4</sub>-POM; spin density maps for the OOH intermediate; DFTderived structures of transition states involved in outer sphere O<sub>2</sub> activation routes; DFT-derived HAE on two-electron reduced H-POM cluster; DFT-derived structures of transition states involved in reactions of OO\* with CH<sub>3</sub>OH; 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 CH<sub>3</sub>OH ODH and C<sub>3</sub>H<sub>6</sub> epoxidation; a comparison of CH<sub>3</sub>-OH ODH and C<sub>3</sub>H<sub>6</sub> 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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