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

Stephanie Kwon [a], Prashant Deshlahra [b], Enrique Iglesia [a,*]

[a] Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720, United States
[b] Department of Chemical and Biological Engineering, Tufts University, Medford, MA 02155, United States

ABSTRACT

Catalytic redox cycles involve dioxygen activation via peroxo (OO*) or H_2O_2 species, denoted as inner-sphere and outer-sphere routes respectively, for metal-oxo catalysts solvated by liquids. On solid oxides, O_2 activation is typically more facile than the reduction part of redox cycles, making kinetic inquiries difficult at steady-state. These steps are examined here for oxidative alkanol dehydrogenation (ODH) by scavenging OO* species with C_3H_6 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* migrations, otherwise required to oxidize non-vicinal vacancies. C_3H_6 epoxidizes by reaction with OO* with rates that increase with C_3H_6 pressure, but reach constant values as all OO* species react with C_3H_6 at high C_3H_6/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_2O, because vacancies, required to form OO*, react with H_2O to form OH pairs and H_2O_2. OO*-mediated routes and epoxidation become favored at low coverages of reduced centers, prevalent for less reactive alkanols and lower alkanol/O_2 ratios, because H_2O_2 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_2O_2 than OO*. These re-oxidation routes prefer molecular donor (H_2O_2) or acceptor (alkanol) to perform stepwise two-electron oxidations by dioxygen, instead of kinetically demanding O-atom migrations. The quantitative descriptions, derived from theory and experiment on Mo-based polyoxometalate clusters with known structures, bring together the dioxygen chemistry in liquid-phase oxidations, including electro-catalysis and monooxygenase enzymes, and oxide surfaces into a common framework, while suggesting a practical process for epoxidation by kinetically coupling with ODH reaction.

1. Introduction

The oxidative dehydrogenation (ODH) and the selective oxidation or epoxidation of organic molecules provide essential routes to convert undervalued streams into marketable chemicals of higher values [1,2]. ODH reactions proceed via Mars-van Krevelen catalytic cycles on reducible metal oxides; these cycles couple the reduction and the re-oxidation of the oxide catalyst via sequences such as the one depicted in Scheme 1 [3,4]. The reduction part involves the abstraction of H-atoms from organic substrates by lattice O-atoms (O*) 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*), 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_2 to re-form oxidized centers (O*), thus completing a catalytic turnover. Re-oxidation steps are fast and thus kinetically-irrelevant in most catalytic oxidations, but can influence the selectivity of these reactions, because O_2-derived intermediates formed during re-oxidation steps can react with organic reactants or products to form undesired side products [10,11]. They are also of fundamental interest in electro-catalysis [12–14] and monooxygenase enzyme systems [15–18],
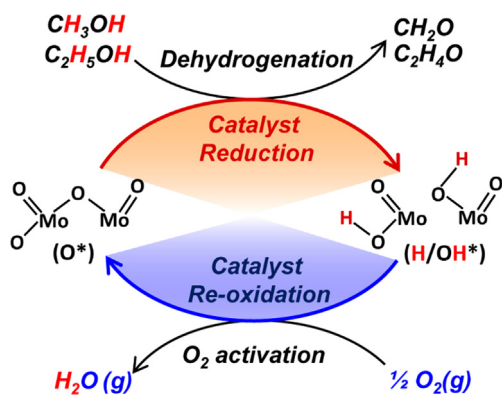
Scheme 1. A Mars-van Krevelen redox cycle involving the reduction of lattice O-atoms (O*) in Mo-based oxide domains via alkanol dehydrogenation steps and re-oxidation of reduced centers (H/OH*) via O_2 activation steps.

which use activated forms of O_2-derived species in the epoxidation of alkenes and the selective oxidation of alkanes.

The fast nature of these re-oxidation pathways renders their dynamics inaccessible to direct experimental inquiry from the kinetic behavior of steady-state ODH catalysis [3]. Re-oxidation rate constants can be indirectly probed through their *in-situ* UV–visible spectra during the transient formation and consumption of reduced centers in response to changes in reductant to oxidant ratios in the reactant streams [19]. Previous studies of propane ODH on supported VO_x-based catalysts indicate that re-oxidation first-order rate constants are 10^3–10^5 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_2 pressure [5–9]. The low surface densities of two-electron reduced centers [19] and their energetically-unfavorable pairing [11] lead to the isolation of such centers during ODH reactions. Their re-oxidation by a four-electron oxidant such as O_2 thus requires the kinetic coupling of two elementary events, each involving one O-atom (and two electrons). Such coupling requires, in turn, the migration of one of the O-atoms in O_2, either via lattice diffusion or via molecular carriers, to react with another reduced center or the decomposition of the O_2-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*) intermediates formed via O_2 activation at O-vacancies (*) with concurrent two-electron re-oxidation of the reduced centers [11,20]. Several sequential diffusional hops by one O-atom in the OO* intermediates formed can bring OO* species near another O-vacancy (*) and re-oxidize the reduced center (*) to form another lattice O-atom (O*), thus completing the required four-electron re-oxidation process using O_2 [11,20]. Such steps involve the cleavage and formation of metal-oxygen (M—O) bonds, in processes that have been denoted "inner sphere" O_2 activation routes in homogeneous systems [14,21,22]. Peroxo-type (OO*) species exhibit detectable UV–visible [23] and Raman [24] features that have been detected during the re-oxidation of reduced CeO_2-based solids by O_2. The detection of bound OO* species, however, is infeasible during ODH catalysis, because reduced centers and O_2-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*) to O_2(g) to form H_2O_2 [12,14,26,27]. Such routes lead to

the appearance of the ^{17}O-atoms in $^{17}O_2$(g) within H_2O_2 and H_2O 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_2 activation routes are quite consequential for alkane ODH selectivity because peroxo (OO*) intermediates, involved in inner sphere O_2 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_2 [10,11,28,29]. The involvement of OO* species in the re-oxidation steps in Mars-van Krevelen ODH cycles and their role in determining product selectivities, however, remain speculative and, for the most part, inaccessible to direct experimental inquiries [10,11].

Here, we provide experimental and theoretical evidence for parallel inner and outer sphere O_2 activation routes during re-oxidation of reduced Mo-based Keggin-type polyoxometalate (POM) clusters and for the presence of OO* 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. Mo-based POM clusters are chosen here as exemplary catalysts because their well-known structure minimizes model uncertainties in benchmarking theory and experiment [3,30], but the methods applied in this work seem general for other redox active metal oxides that involve parallel inner and outer sphere O_2 activation routes. CH_3OH and C_2H_5OH 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* 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 O_2 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_2O_2 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_2 (Cab-O-Sil; 304 m^2 g^{-1}; 1.5 cm^3 g^{-1} pore volume) as a mesoporous support. SiO_2 support was rinsed three times with 1 M HNO_3 (10 cm^3 g-SiO_2^{-1}) to remove any impurities and then treated in flowing dry air (UHP Praxair, 0.83 cm^3 g^{-1} s^{-1}) 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^{-2}. Impregnated samples were kept in closed vials at ambient temperature for 24 h and then treated in flowing He (99.999%, Praxair, 0.83 cm^3 g^{-1} s^{-1}) at 323 K for 24 h. The powders were then pressed into pellets, crushed, and sieved to retain 106–180 μm aggregates. Transmission electron microscopy showed that POM clusters after synthesis (and also after CH_3OH ODH reactions) were predominantly present