

# MECHANISTIC DETAILS OF CATALYTIC REDOX PROCESSES DURING ALKANOL-O<sub>2</sub> REACTIONS ON OXIDES: EXPERIMENT AND THEORY

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## Abstract

Details of the elementary steps that mediate reduction and re-oxidation of oxides in redox cycles for CH<sub>3</sub>OH oxidative dehydrogenation (ODH) catalysis on polyoxometalate clusters are probed using kinetic and isotopic measurements, UV-visible spectroscopy and density functional theory calculations. The kinetically-relevant reaction step involves direct C-H activation of CH<sub>3</sub>OH molecule, leading to dehydrogenated formaldehyde product and hydroxylated reduced oxide. The reduced surface is re-oxidized via rapid steps involving O<sub>2</sub> activation at surface hydroxyls to form hydroperoxide species or those involving desorption of hydroxyls and subsequent O<sub>2</sub> activation at O-vacancies. Re-oxidation of isolated reduced centers by O<sub>2</sub> via both hydroperoxide and vacancy routes leads to surface peroxides. The presence of such peroxides and the dynamics of their formation and consumption were probed by co-feeding C<sub>3</sub>H<sub>6</sub> during CH<sub>3</sub>OH-O<sub>2</sub> reactions because C<sub>3</sub>H<sub>6</sub> molecules form epoxidation products selectively at such surface peroxides.

## Keywords

Redox catalysis, Oxidative dehydrogenation, epoxidation, oxide clusters, heteropolyacids.

## Introduction

Polyoxometalate (POM) clusters are oxides with a known Keggin type structure. They consist of central tetrahedral oxoanions encapsulated in a metal oxide shell with twelve metal atoms protons embedded on the shell to balance the charge on oxo-anions [H<sub>8-n</sub> (X<sup>n+</sup>O<sub>4</sub>)(M<sub>12</sub>O<sub>36</sub>); X= P, Si, Al, Co, M = W, Mo, V etc.] (Pope and Muller, 1991). Protons act as Brønsted acid sites, while MO<sub>x</sub> domains can undergo redox cycles to catalyze oxidative dehydrogenation (ODH) or organic molecules. The known Keggin structure of these materials allows reliable calculation of their properties using density functional theory (DFT) and rigorous comparison of kinetic and isotopic and spectroscopic studies with calculated energies of intermediate and transition states involved in relevant elementary steps. Here, we report such studies to probe mechanistic details of catalyst reduction and re-oxidation

steps involved in reactions CH<sub>3</sub>OH-O<sub>2</sub> mixtures on Mo-based POM clusters.

## Materials and methods

POM clusters were supported on silica using incipient wetness impregnation. Solid state NMR, TEM and titration of acid sites with 2,6-ditertbutylpyridine were used to probe catalyst structure and accessibility of reactive sites to reactant molecules (Deshlahra et al., 2015). *In-situ* UV-visible spectra were used to measure ligand-to-metal charge transition energies of oxidized POM cluster and intensities of spectral features that represent d-d transitions in reduced centers with partially filled d-electrons that are generated during catalysis. Energies of intermediates and transition states for POM reduction and re-oxidation steps were derived from DFT

and hybrid-DFT calculations in Vienna *ab-initio* simulation package and Gaussian program.

## Results and discussion

ODH reactions involve cyclic reduction and re-oxidation of oxides in kinetically coupled elementary steps (Mars and van Krevelen, 1954). CH<sub>3</sub>OH ODH rates changed linearly with CH<sub>3</sub>OH pressure at low pressures, and showed weaker sublinear dependence as pressure increased; this Langmuir-type behavior suggests saturation of oxide surface with adsorbed CH<sub>3</sub>OH with increasing pressure. First-order rate constant obtained from rate data ( $k_{1st,ODH}$ ) reflect stability of kinetically relevant transition state with respect to gaseous CH<sub>3</sub>OH. Measured kinetic isotope effects ( $r_{CH_3OH}/r_{CD_3OD} = 2.5$ ,  $r_{CH_3OH}/r_{CH_3OD} = 1.0$ ) suggest that this transition state involves H-abstraction from C-H bond of CH<sub>3</sub>OH, but such measurements cannot discern between H-abstraction a CH<sub>3</sub>OH molecule and that from a dissociated methoxy species; the latter are typically presumed to be prevalent despite lacking spectroscopic evidence of reactive methoxides on several oxide surfaces during ODH conditions. DFT calculations can distinguish between the molecular and the dissociative routes, and we show that H-abstraction from molecularly adsorbed CH<sub>3</sub>OH are significantly more favorable than dissociative route and its calculated pathways are consistent with experimental kinetic and isotopic measurements (Deshlahra and Iglesia, 2014). ODH rates were independent of O<sub>2</sub> pressure and adding H<sub>2</sub>O to CH<sub>3</sub>OH-O<sub>2</sub> reactant mixtures decreased rates without changing O<sub>2</sub> pressure dependence, suggesting that re-oxidation steps are of rapid nature and, as a result, the terms in rate equations representing concentrations of reduced centers are negligible. These results also suggest that H<sub>2</sub>O inhibits ODH rates by decreasing surface concentration of adsorbed CH<sub>3</sub>OH via competitive adsorption.

Re-oxidation of reduced POM clusters is kinetically silent but their details are relevant to elementary steps that complete the redox turnovers and are accessible through detection of reduced centers in UV-vis spectra. Spectra from experiments and time dependent DFT calculations suggest that the extent of reduction during catalysis remains small; the concentration of reduced centers decreases with increasing O<sub>2</sub> and H<sub>2</sub>O pressures, which is consistent with increased re-oxidation rates and with blocking of oxidized centers by H<sub>2</sub>O. DFT calculation show that re-oxidation steps can proceed via a pathway involving O-vacancy formation in reduced cluster followed by O<sub>2</sub> activation at the vacancy, and a second pathway involving formation hydroperoxide radicals by direct reaction of O<sub>2</sub> with the H-atom in the reduced cluster without vacancy formation; prevalence of the two routes is determined by H<sub>2</sub>O concentration in the gas-phase because higher H<sub>2</sub>O pressures decrease O-vacancy concentrations and favor hydroperoxide routes. Low extents of reduction during catalysis suggest that reduced centers in oxides are far from each other. Re-oxidation of

an isolated reduced center (single vacancy or a surface hydroxyl pair) by two O-atoms of O<sub>2</sub> molecule inevitably leads to formation of surface peroxide species. These peroxide species either re-oxidize another reduced center on the cluster or directly react with gaseous molecules. The low steady-state concentration of such peroxide, while undetectable from spectroscopy, can be probed using co-feeding propene, which selectively reacts with such peroxides to form epoxides (Liu et al., 2004). The measured changes in epoxidation rates with ODH rates, propene and O<sub>2</sub> pressure are consistent with the proposed elementary steps for re-oxidation mechanism of reduced clusters and with energies of intermediates and transition states determined from DFT.

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