



Priority Communication

Method for quantifying redox site densities in metal oxide catalysts: Application to the comparison of turnover frequencies for ethanol oxidative dehydrogenation over alumina-supported VO_x , MoO_x , and WO_x catalysts

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ABSTRACT

Isothermal anaerobic titration with ethanol as a probe molecule is proposed as an accurate technique to quantify active redox site densities in supported metal oxide catalysts. It is shown that the number of active redox sites for $\text{VO}_x\text{-Al}_2\text{O}_3$, $\text{MoO}_x\text{-Al}_2\text{O}_3$, and $\text{WO}_x\text{-Al}_2\text{O}_3$ catalysts is a function of both the metal atom and its oxide surface density, but the intrinsic redox rate per active site is independent of both of these factors. Thus, the difference in steady-state redox rates per metal atom is due only to differences in the number of redox sites under reaction conditions.

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1. Introduction

The ability to identify and quantify active redox sites in metal oxide catalysts is critical for determining accurate turnover frequencies for redox reactions, which in turn are required to accurately compare the performance and reaction mechanism over catalysts of different structure and composition. For supported metal oxide catalysts, it has become convention to report the turnover rate *per metal atom*, though this is known to be only an approximation for the turnover frequency, because the rate per metal atom strongly depends on such factors as the metal oxide surface density, local structure, and reaction conditions.

Numerous probe methods have been used in efforts to quantify the density of sites available on supported and bulk oxide catalysts for partial oxidation and oxidative dehydrogenation reactions. Methanol has commonly been used to gain insight into both the function and density of active sites on transition metal oxide catalysts [1–3], because products from steady-state methanol oxidation indicate the relative redox, acidic, and basic character of the catalyst surface. Isothermal methanol uptake measurements have been used to approximate the number of active sites available for

methanol reactions; however, such uptakes distinguish neither active sites from inactive chemisorption sites nor redox sites from acid/base sites [4]. Temperature-programmed surface reactions after methanol chemisorption have been used to quantify the density of redox and acid sites; however, the nonisothermal nature of this method is not ideal, because both surface coverage and metal oxide reducibility are likely affected by temperature [5].

The number of terminal vanadyl species ($\text{V}=\text{O}$) in supported vanadium oxide catalysts has been measured using reactions with NO and NH_3 [6,7] and also by O-atom exchange between ^{18}O -labeled acetone and $\text{V}=\text{O}$ sites [8]. But these two techniques are applicable only for cases where the active site is associated with a terminal metal–oxygen bond. Although oxygen chemisorption after prereluction in H_2 often has been used as redox site probe [9–12], both the prereluction step and the chemisorption step are highly sensitive to temperature. Bulk reduction of the oxide during high-temperature chemisorption and physisorbed oxygen during low-temperature chemisorption can lead to incorrect estimates of the number of redox sites. In addition, the local structure and surface properties of metal oxide catalysts depend strongly on the environment [13]. Thus, the number of active sites available on a catalyst surface will vary significantly and can be measured only during a chemical reaction.

In this study, we demonstrate the use of anaerobic reactions to count the number of redox sites on alumina-supported oxide cat-

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alysts of molybdenum, tungsten, and vanadium. Using ethanol as a model reactant, the number of active redox sites for ethanol oxidative dehydrogenation to acetaldehyde at 453 K is determined by anaerobic reaction at 453 K, during which oxygen is removed from the reactant stream and the transient decay in activity from steady state is monitored. Ethanol oxidation to acetaldehyde is known to occur through a Mars–van Krevelen-type mechanism using oxygen from the catalyst surface. Reoxidation of the catalytic sites reduced by ethanol can be suppressed if oxygen is not present in the reactant stream. Thus, the presented anaerobic reaction method is a stoichiometric titration, during which each molecule of acetaldehyde produced after oxygen removal has a direct correspondence to the number of active redox sites available at the surface. Only active redox sites are counted, because redox product formation is used for the quantification. This is in contrast to ethanol chemisorption techniques, which quantify the total surface coverage of ethanol, some of which reacts via a redox path to form acetaldehyde and some of which reacts via an acid-catalyzed pathway to form diethyl ether (at 453 K). In principle, this methodology of anaerobic titration for estimating active redox site densities on metal oxides catalysts using the reactant as the probe molecule can be extended to any similar oxidation or oxidative dehydrogenation reaction using lattice oxygen in the catalytic cycle. This technique of measuring redox site density should be extremely accurate, because the reactant is used as the probe molecule and active sites are measured at reaction temperature with all conditions similar except for the presence of oxygen in the gas phase.

2. Experimental

2.1. Catalyst preparation

Alumina-supported catalysts containing tungsten oxide ($\text{WO}_x\text{-Al}_2\text{O}_3$), molybdenum oxide ($\text{MoO}_x\text{-Al}_2\text{O}_3$), and vanadium oxide ($\text{VO}_x\text{-Al}_2\text{O}_3$) with surface densities varying from 0.5 to 8 metal atoms/ nm^2 were prepared by incipient wetness impregnation of γ -alumina (Alcoa 151 m^2/g , 98.8%) with aqueous solutions of ammonium tungsten oxide (Alfa Aesar, 99.999%), ammonium molybdate (Alfa Aesar, 99.999%), and ammonium vanadium oxide (Alfa Aesar, 99.995%), respectively. Oxalic acid, at an oxalic acid: precursor weight ratio of 2:1, was used to aid dissolution of the precursor at higher loadings. Metal atom surface densities were based on the initial alumina surface area available for impregnation (151 m^2/g). BET results obtained by N_2 physisorption at 77 K on a Micromeritics ASAP 2000 instrument confirm that the surface area did not decrease significantly at the surface densities studied here, as also was shown in previous studies [14]. Catalysts were dried overnight at 393 K and then calcined in flowing air (zero grade, 0.5 cm^3/s) at 923 K (0.33 K/s) for 3 h.

UV–visible spectroscopy was used to confirm good dispersion and domain growth of supported catalysts with increasing surface density. UV–vis methods and results for the catalysts in this paper have been reported previously [15]. Absorption edge energies decreased with increasing surface density, confirming that oxide domain size systematically increased with increasing surface density.

2.2. Ethanol reaction

The activity and selectivity of prepared catalysts were measured using continuous-flow, fixed-bed, vertical U-tube quartz reactors containing ~ 0.025 g of catalyst (125–250 μm particles) dispersed on a quartz frit. Before reaction, all samples were treated in 1.67 cm^3/s of simulated air (22% O_2/He) at 773 K for 2 h. Reactions were carried out at 453 K with a total gas flow rate of 0.83 cm^3/s . A constant partial pressure of 0.5 kPa ethanol and 1.5 kPa oxygen

was maintained in the reactant stream through controlled injection of liquid ethanol (0.000022 cm^3/s , AAPER, absolute 200 proof) into a flowing mixture of oxygen and helium with a Cole Palmer single-syringe infusion pump (EW-74900-00). Reactant and product concentrations were measured using the thermal conductivity detector of an Agilent 3000A micro gas chromatograph (HP-PLOT Q column).

Anaerobic reactions were carried out to measure the amount of lattice oxygen available to ethanol during reaction. Oxygen was removed from the reactant stream using a 4-port Valco switching valve under total reactant flow rates and ethanol partial pressure identical to those under steady-state reaction conditions. Acetaldehyde and ether formation were monitored simultaneously using a combination of a Hiden Analytical HPR20 mass spectrometer and an Agilent 3000A micro gas chromatograph (PlotQ column). Intensities at m/e of 44 (acetaldehyde) and 59 (diethyl ether) were used in conjunction with the micro gas chromatograph to quantify product formation rates as a function of time. The rate of acetaldehyde formation is known to decay with time once oxygen is cut off in the reactant stream. Rapid mass spectrometry analysis indicated that the oxygen in the outlet stream was reduced to zero almost immediately after it was removed from the feed.

Activation energies for alumina-supported Mo, W, and V catalysts with surface densities of 8 metal atoms/ nm^2 were obtained from Arrhenius plots using acetaldehyde formation rates from steady-state reaction at 443 K, 453 K, and 463 K. This narrow temperature range was chosen to obtain an accurate estimate of the activation energy at 453 K without disturbing either the catalyst selectivity or the number of redox sites on the catalyst observed with more drastic changes in temperature. Error estimates for activation energies are based on 95% confidence intervals.

3. Results and discussion

Reaction of ethanol at 453 K over all supported molybdenum, tungsten, and vanadium oxide catalysts led to the formation of both acetaldehyde via oxidative dehydrogenation and diethyl ether via dehydration on what can be classified as redox and acid sites, respectively. Product selectivity is independent of conversion over the range studied (<10% conversion) and is representative of the relative redox and acidic character of the catalyst. Diethyl ether is the only product formed over alumina; thus, reactions on the support should not affect the quantification of redox sites.

Fig. 1 shows rates of acetaldehyde (redox product) formation per metal atom as a function of surface density for $\text{WO}_x\text{-Al}_2\text{O}_3$, $\text{MoO}_x\text{-Al}_2\text{O}_3$, and $\text{VO}_x\text{-Al}_2\text{O}_3$ catalysts. Acetaldehyde formation rates were substantially lower over acidic $\text{WO}_x\text{-Al}_2\text{O}_3$ than over the more reducible $\text{MoO}_x\text{-Al}_2\text{O}_3$ and $\text{VO}_x\text{-Al}_2\text{O}_3$ catalysts. Acetaldehyde formation rates varied with surface density and showed slight maxima near the reported monolayer coverage for $\text{MoO}_x\text{-Al}_2\text{O}_3$ (~ 4 atoms/ nm^2) and $\text{VO}_x\text{-Al}_2\text{O}_3$ (~ 8 atoms/ nm^2) [16]. This observed maximum in the oxidative dehydrogenation rate per metal atom near monolayer coverage has been attributed to a required balance between oxide domain reducibility (which increases with increasing surface density) and oxide domain accessibility (which decreases with increasing surface density beyond monolayer capacity) [17].

Using total metal atoms to calculate the turnover frequency is known to be an incorrect approach, because each metal site does not act as an active site for ethanol oxidation [18,19]. To properly identify the density of active redox sites for ethanol oxidative dehydrogenation, the reaction mechanism, which parallels that of methanol, must be taken into account [18,19]. Ethanol initially adsorbs as an ethoxy species that can then form either acetaldehyde or diethyl ether. The main difference in the mechanistic pathways for the two products is the use of lattice oxygen. Acetaldehyde

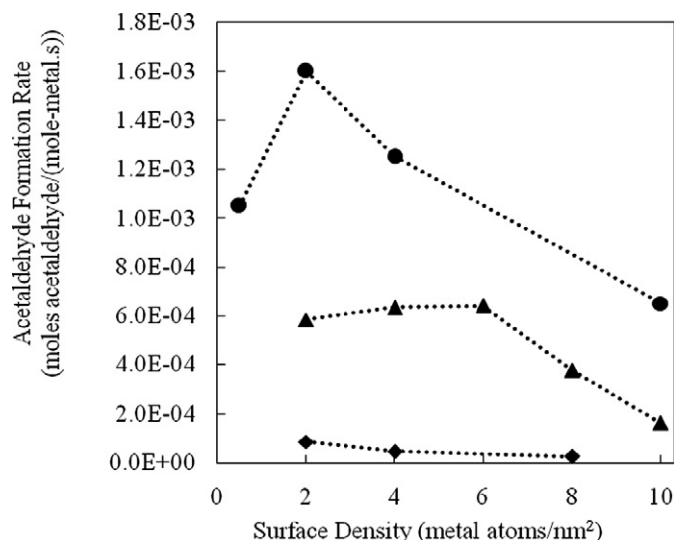


Fig. 1. Rate of acetaldehyde formation at 453 K as a function of surface density for MoO_x-Al₂O₃ (●), WO_x-Al₂O₃ (◆) and VO_x-Al₂O₃ (▲).

formation proceeds through a Mars-van Krevelen-type mechanism and is coincident with removal of oxygen from the catalyst surface (which is subsequently reoxidized using gas-phase O₂). In the absence of oxygen, each molecule of acetaldehyde produced corresponds to a redox site available for reaction at the operating temperature.

Fig. 2a shows the rate of formation of acetaldehyde and ether over a MoO_x-Al₂O₃ catalyst with 2 Mo atoms/nm² at steady state and then after O₂ was removed from the reactant gas (at time 0). Acetaldehyde rates decreased under anaerobic conditions due to depletion of oxygen from the catalyst; diethyl ether formation rates were invariant, because lattice oxygen was not required for ether formation. Acetaldehyde formation rates did not diminish completely to zero. It was verified that this was not due to reoxidation with water vapor, but rather resulted from very small oxygen leaks in the system (calculated as <100 ppm) and oxygen diffusion from the bulk alumina support.

The number of active redox sites available to ethanol under reaction conditions can be quantified by integrating the diminishing rate of acetaldehyde formation over time (the shaded area in Fig. 2a). For all catalysts, the rate exhibited a nearly first-order dependence on the number of active sites remaining (rate_{AC} = k[O*]ⁿ), where *n* was measured from linear regression in the range of 0.5–1, and remained constant over the area of integration. This power law model observed experimentally during the anaerobic titrations confirms that deactivation of one redox site (oxygen removal) had no effect on the density or accessibility of neighboring redox sites.

A linear dependence of the redox rate on active O* sites can be predicted from a proposed mechanism for ethanol oxidation [20], wherein the rate-determining step is the abstraction of an H atom from C in an adsorbed ethoxy species to an active O* site, as shown in (1) and (2):



Here EtOH represents an ethanol molecule, M represents a metal atom, EtO-M represents an adsorbed ethoxy, Ac-M represents an adsorbed acetaldehyde, and O* is a lattice oxygen.

The rate for AcH formation then can be expressed as given in (3), where *z* is the probability that the adsorbed ethoxy has

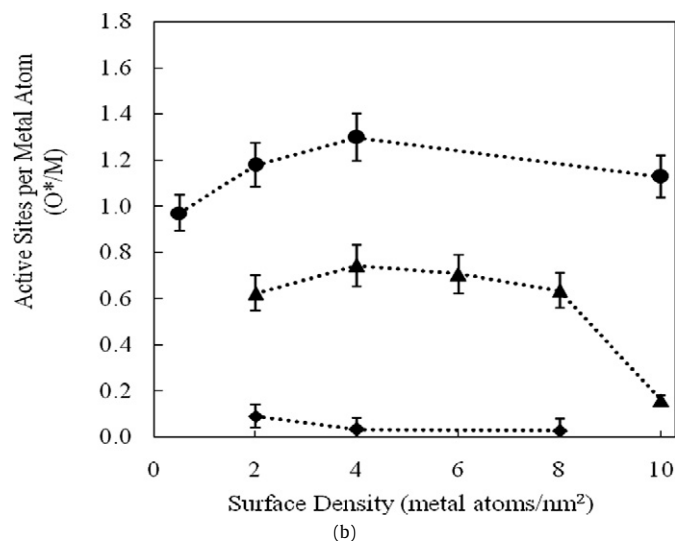
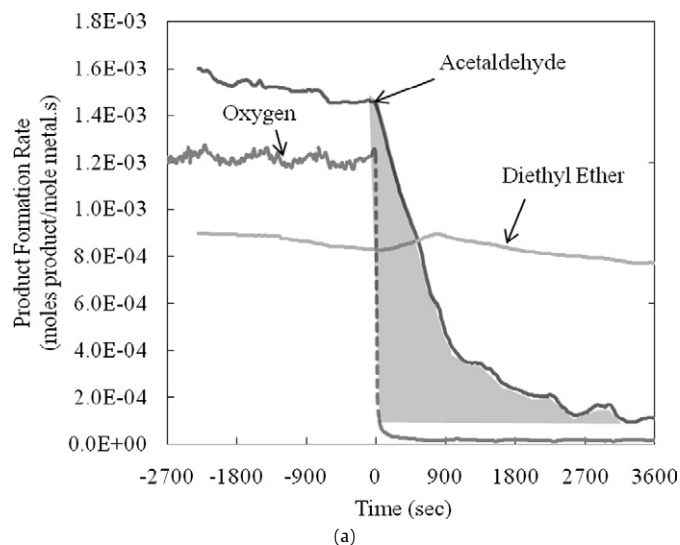


Fig. 2. (a) Rate of Acetaldehyde and Ether formation at 453 K as a function of time for 2 Mo catalyst before and after O₂ is removed from the reactant feed (the O₂ decay is shown with arbitrary units). (b) Number of active redox sites at 453 K as a function of surface density for MoO_x-Al₂O₃ (●), WO_x-Al₂O₃ (▼) and VO_x-Al₂O₃ (▲). Error bars reflect 95% confidence intervals based on multiple measurements of the number of active sites.

a removable oxygen next to it and [EtO-M]/[M] is the fractional ethoxy coverage (θ_{Et}):

$$r_{\text{AC}} = k_2 [\text{EtO-M}] [\text{O}^*] (z) / [\text{M}]. \quad (3)$$

From this, it is clear that $r_{\text{AC}} \sim [\text{O}^*] (z)$, which is the effective value measured by the anaerobic titration.

In the anaerobic experiments, only lattice oxygen atoms that can be removed by ethanol at reaction conditions were measured. Fig. 2b shows the density of these redox sites per metal atom as a function of surface density for WO_x-Al₂O₃, MoO_x-Al₂O₃, and VO_x-Al₂O₃ catalysts. Redox site densities were approximately 0.1 O*/W-atom for the WO_x catalysts, 0.7 O*/V-atom for the VO_x catalysts, and 1.2 O*/Mo-atom for the MoO_x catalyst. The MoO_x-Al₂O₃ catalysts showed an apparent availability of >1 O*/M-atom for catalysts with 2 and 4 Mo/nm²; however, the density at steady-state reaction conditions was limited by the maximum ethoxy coverage, expected to be 1 per metal atom. In this situation, acetaldehyde production was limited not necessarily by the number of redox sites, but rather by the number of adsorption sites. Under anaerobic conditions, multiple adsorptions on the same site apparently

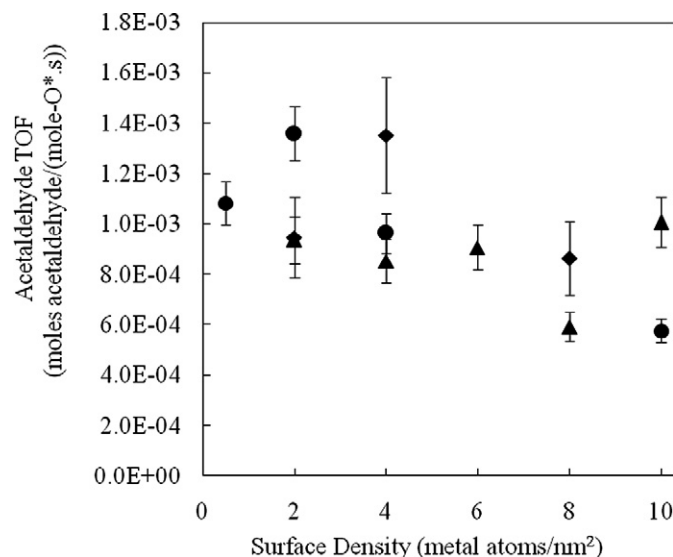


Fig. 3. Acetaldehyde formation rates for $\text{MoO}_x\text{-Al}_2\text{O}_3$ (■), $\text{WO}_x\text{-Al}_2\text{O}_3$ (●) and $\text{VO}_x\text{-Al}_2\text{O}_3$ (▲). Error bars reflect 95% confidence intervals based on multiple measurements of the number of active sites.

led to the removal of oxygen that would not necessarily be removed under steady-state conditions. This phenomenon, combined with experimental error in measuring O^* , led to titration values slightly above 1 for the MoO_x catalysts.

Fig. 2 shows that the redox site density was clearly a function of both the surface density and the metal atom, two factors that affect the reducibility and accessibility of M-O bonds. Two independent parameters were measured during the anaerobic titrations: acetaldehyde formation rate and total number of redox sites. The two are related by the time for complete titration of the redox sites—a characteristic decay time. Catalysts with high acetaldehyde production rates (per metal atom) had longer characteristic decay times (despite the high rates), whereas catalysts with smaller acetaldehyde production rates had shorter decay times.

Fig. 3 shows redox turnover frequencies, reported as the acetaldehyde formation rate per redox site obtained from anaerobic titration. As shown, the redox turnover frequencies over all alumina-supported MoO_x , VO_x , and WO_x catalysts were similar and did not depend on either the transition metal or the surface density. The finding that intrinsic turnover frequencies were independent of both the nature and amount of metal oxide on the alumina support has profound implications. The rates per metal atom over supported VO_x , MoO_x , and WO_x catalysts differed markedly because of the differing density of available redox sites (removable O^* sites) in each. Although the reducibility of the oxide likely played a strong role in determining this density, the specific reaction rate over each active site did not appear to be a factor.

This result also could be predicted by the mechanism outlined earlier. The rate per active site can be expressed as

$$r_{\text{AC}}/([\text{O}^*](z)) = k_2 \theta_{\text{Et}}. \quad (4)$$

Assuming that each metal atom can adsorb only one ethanol molecule and that the ethanol coverage is 1 at 453 K, the rate of acetaldehyde formation measured per active redox site is the rate

constant k_2 . Our results suggest that this rate constant k_2 was the same for all catalysts, and that it represents the rate-determining C–H activation. The following activation energies were measured: 23 ± 5 kcal/mol on $\text{VO}_x\text{-Al}_2\text{O}_3$ (8 V/nm^2), 20.5 ± 5 kcal/mol on $\text{MoO}_x\text{-Al}_2\text{O}_3$ (8 Mo/nm^2), and 17 ± 7 kcal/mol on $\text{WO}_x\text{-Al}_2\text{O}_3$ (8 W/nm^2). These values are similar to those reported previously for methanol oxidation over similar catalysts [21,22]. The similar activation energies in these catalysts supports the observation that intrinsic turnover frequencies also are the same on these catalysts.

4. Conclusion

We have demonstrated the use of anaerobic reactions with ethanol to quantify active redox sites for alcohol oxidation on alumina-supported molybdenum, tungsten, and vanadium oxide catalysts. These titrations gave an accurate representation of the number of active sites available to the reactant molecule under reaction conditions by incorporating the effects of both active site reducibility and accessibility. Normalization of acetaldehyde formation rates using the number of active sites determined by the anaerobic titration technique indicated that redox rates on alumina-supported oxide catalysts had very little dependence on either the nature of the metal oxide or the surface density. Turnover rates for $\text{VO}_x\text{-Al}_2\text{O}_3$, $\text{MoO}_x\text{-Al}_2\text{O}_3$, and $\text{WO}_x\text{-Al}_2\text{O}_3$ were indistinguishable within the limits of experimental error, and trends in rate with surface density were absent.

Supplementary information

Supplementary information for this article may be found on ScienceDirect, in the online version.

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