The dissociation-induced displacement of chemisorbed O₂ by mobile O atoms and the autocatalytic recombination of O due to chain fragmentation on Ag(110)

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Abstract:

The interplay between thermal desorption of chemisorbed dioxygen and its dissociation was studied with temperature programmed methods. Analysis of the kinetics of molecular desorption and the fraction of adsorbed molecules which dissociate is consistent with a model in which oxygen atoms released by the dissociation event induce desorption of the molecular species. These unequilibrated atoms exhibit a mean free path relative to the chemisorbed dioxygen of 1.8 nm prior to thermalization with the surface, displacing chemisorbed dioxygen within their reach. Each dissociation event leads to desorption of two oxygen molecules if the space between chemisorbed molecules approaches the minimum of 0.58 nm. This condition can be achieved experimentally by saturating the population of chemisorbed dioxygen (0.33 ML O₂) at 90 -100 K. Oxygen adatoms recombine near 580 K from the reconstructed (nx1)-O adlayer with kinetics dictated by progressive fragmentation of the $O(AgO)_m$ rows. This behavior gives rise to autocatalytic recombination kinetics of oxygen adatoms which produces both an acceleration of

rate at constant temperature and unusual recombination kinetics in temperature programmed desorption.

Introduction

Amongst the noble metals, pristine silver occupies a unique niche in its surface reactivity, providing an active channel for the dissociation of dioxygen, while remaining relatively inert to C-H, C-C, and O-H bond activation. Silver provides a good catalytic substrate for many heterogeneous industrial processes, such as the selective partial oxidation of methanol to formaldehyde. This selectivity emerges from the confluence of two factors: 1) the effectively complete dominance of oxygen-mediated reaction pathways over silver-adsorbate interactions and 2) the relatively weak silver-oxygen bond. All selective silver-catalyzed partial oxidation reactions are oxygen-activated by nature. Understanding the nature of the dioxygen dissociation process, the metal-oxygen bond characteristics, and the reactivity of the various species of adsorbed oxygen provides deeper insight into the mechanisms underlying these reactions.

The importance of this understanding is particularly relevant to the elucidation of oxygen-assisted catalytic reactions over nanoporous gold (npAu).[1,2] This material has been shown recently to effectively catalyze the vapor phase coupling of alcohols at atmospheric pressure and relatively low temperatures. npAu is actually a dilute alloy of silver in gold,[3] and it is believed that low concentrations of silver at the surface activate dioxygen, subsequent reactions occurring between the alcohols and atomic oxygen which migrates onto the (predominantly) gold surface.

Dioxygen *chemisorbs* on the Ag(110) surface at temperatures below 160 K.[4,5] The oxygen molecules are located within the troughs of the Ag(110) surface, their molecular axis being oriented parallel to the surface along the $[1\bar{1}0]$ direction; the oxygen molecules are bound to the surface in a peroxo configuration. A strong bond is formed with the surface due to electron

donation from the surface into the antibonding pi-orbitals, resulting in reduction of the O-O bond order from two to one. Upon annealing, dioxygen spontaneously dissociates at 160 K, and a fraction of the adsorbed dioxygen concurrently desorbs, as confirmed through $^{18}\text{O}_2/^{16}\text{O}_2$ coadsorption experiments, which show no isotopic mixing in the low temperature states (Eqns. 1 and 2).[5]

The oxygen adatoms, $\text{O}_{(\text{a})}$, subsequently form an (nx1) added-row reconstruction, incorporating silver atoms from step sites to form extended chains of $\text{O}\{\text{AgO}\}_m$ along the [001] direction. [6-9] Values of ‘n’ have been observed with low energy electron diffraction (LEED) ranging from eight at low coverages of oxygen adatoms to two at the saturation coverage of 0.50 ML $\text{O}_{(\text{a})}$. Strong attractive interactions provide stabilization of the rows in the [001] orientation, while long-range repulsive interactions exist in the $[1\bar{1}0]$ direction between the chains. The added-row reconstruction is stable until about 530 K, when the rows decompose, allowing for the recombination of dioxygen (Eqn. 3).[7]

STM experiments at low coverage indicate that associatively adsorbed dioxygen tends to form dispersed chains within the $[1\bar{1}0]$ -oriented troughs of the (110) crystal face at temperatures low enough to suppress mobility ($< 100 \text{ K}$). The molecules within these chains experience strong nearest-neighbor repulsions as well as weak long-range attractive interactions between next-nearest neighbors in the $[1\bar{1}0]$ direction and weaker diagonal coupling in the [001]

crystallographic orientation.[10,11] At higher temperatures, but below the temperature at which the molecules dissociate (< 145 K), chemisorbed dioxygen is more mobile.

In addition to the dioxygen desorption and recombination pathways, CO and CO₂ are known to react with molecular oxygen at low temperatures (Eqns. 4 – 6). The production of surface carbonate occurs via reaction of both molecular and atomic oxygen on the Ag(110) surface:[12,13]

Carbonate itself decomposes at 460 K (Eqn. 7).

Water also reacts with atomic oxygen adsorbed on the Ag(110) surface to form hydroxyls (Eqn. 8)[14-16]

which recombine at 314 K (Eqn. 9.)

The released oxygen adatom incorporates into the $\text{O}(\text{AgO})_m$ reconstruction above 200 K.[11,17]

Because of the importance of understanding dioxygen activation on nanoporous Au, we have reexamined both the desorption of dioxygen at low temperature and the recombination of adsorbed oxygen near 580 K, developing a mechanism that explains the molecular desorption process as well as the complexities of the atomic recombination. Related studies on npAu will be reported separately.

Experimental:

All experiments were conducted in an ultra high vacuum (UHV) chamber with a base pressure in the mid 10^{-10} Torr range. The Ag(110) single crystal was cleaned with repeated cycles of Ar^+ sputtering and annealing to 950 K. Carbon contamination of the surface was removed by prolonged exposure to O_2 (5×10^{-6} Torr, directly dosed) at 500 K. Surface purity was confirmed by the absence of CO_2 traces originating from the samples when heated after exposure of the surface to oxygen as well as by X-ray photoelectron spectroscopy (SPECS EA-200). Mass spectrometry data were collected during temperature programmed heating with a quadrupole mass spectrometer (Hiden Hal201). The sample was placed in direct line of sight of the 4 mm aperture of the mass spectrometer shroud; no other elements of the sample manipulator assembly (in particular the sample heating filament) were in direct line of sight of the mass spectrometer.

Sample temperature was controlled with a Eurotherm 800 controller. All temperature programs were conducted at 5 K sec^{-1} , unless otherwise noted. Cooling was accomplished through direct thermal coupling of the sample to a liquid nitrogen cold finger with a lowest attainable temperature of 80 K. All reactions, regardless of the initial static sample temperature, were examined with system cooling operative.

The oxygen scavenging reactions noted above (Eqns. 4 – 6, 8) can obscure the overall population of adsorbed molecular and atomic oxygen observed in temperature programmed desorption (TPD) by converting a fraction of the adsorbed molecules to atomic oxygen, which thereby contribute to the recombination channel, or by direct reaction with atomic oxygen (though each of these reactions can be separately monitored and quantitative corrections made). Application of a dry-ice cold trap to the oxygen gas dosing lines minimized water and CO contamination during dosing. The dioxygen dosage was regulated by a needle valve, and the sample surface was placed directly in front of the oxygen-dosing nozzle for an enhancement factor of 50 relative to the background increase in pressure. For $O_{(a)}$ saturation of the surface (under UHV conditions) dioxygen was dosed for 5 min at a background pressure of 5×10^{-6} Torr. During dioxygen direct dosing exposures, all hot filaments were extinguished to reduce background generation of CO and CO₂. In some experiments clear evidence for a minor amount of reactions (6) and (8) was observed. In these instances any adsorbed atomic oxygen consumed in the reaction is regenerated by reactions (7) and (9) and is ultimately incorporated into the high temperature O-atom recombination peak. Experiments in which evidence for significant contributions from reactions (4) and (5) was obtained were discarded due to the effect of oxygen scavenging on the computed branching ratios (compare Fig. S1 in the supplemental information). All factors considered, the maximum error in the integrated oxygen peak intensity was $\leq 10\%$. The crystal was maintained at 300K during dioxygen exposure for experiments in which the dioxygen recombination pathway was examined exclusively. Coverages were referenced by integrating TPD areas to saturation coverage of 0.50 ML O (4×10^{14} atoms/cm²) in the desorption state at 580 K.[7]

Results:

Exposure of Ag(110) to O₂ at 90 K and 100 K leads to three distinct O₂ desorption peaks in temperature programmed desorption experiments; the sample temperature during dosing and the amount of oxygen dosed determine the relative intensities of the peaks. Dosing of O₂ onto Ag(110) at 90 K or 100 K results in desorption peaks at 120 K, 160 K and 580 K (Fig. 1). The low temperature desorption peaks result from the desorption of intact O₂ molecules, whereas the peak at 580 K results from the recombination of dissociated oxygen.[5] The desorption peak at 120K is significantly populated only if adsorption is conducted below 100 K, because at this temperature there is already a competition between adsorption and desorption. The observed populations of the 160 K state of 0.36 ML O_(a) (0.18 ML O_{2(a)}) at 100 K and 0.40 ML O_(a) (0.20 ML O_{2(a)}) at 90 K significantly exceed the saturation coverage of 0.24 ML O_(a) (0.12 ML O_{2(a)}) reported previously for adsorption at 126 K.[5] These coverages correspond to saturation of this state; higher doses of O₂ increased the peak at 120 K, but not the 160 K peak. The same holds true for the peak at 580 K which saturated at 0.16 ML O_(a) at 100 K (90 K), irrespective of any further increases in the 120 K state. The maximum amount of adsorbed oxygen contained in the 160 K and 580 K thus adds up to 0.52 ML following adsorption at 100 K (0.56 ML at 90K). The peaks at both 160 and 580 K saturate in magnitude before the state at 120 K grows significantly. Literature also reports on the existence of several more adsorption states of O₂ on Ag(110) in a temperature range below 80 K.[18]

Figure 1: Temperature-programmed desorption spectra of dioxygen for an exposure of 75000 L at 90 K and 100 K on Ag(110). In addition to the 160 K molecular desorption and 580 K recombinative desorption states, an additional molecular desorption state is observed at 120 K. Further population of the state at 120 K influences neither the 160 K nor the 580 K state. The fitted peaks only serve as a guide for the eye.

Figure 2: Experimental desorption spectra of dioxygen for progressive O_2 exposures at 125 K between 400 L and 75000 L (top) resulting in total $O_{2(a)}$ coverages of 0.025, 0.12, 0.16, 0.19, and 0.23 ML. At higher exposures the onset of desorption occurs at lower temperatures. Simulated desorption spectra (bottom) were obtained from a hot atom displacement kinetic model for total $O_{2(a)}$ coverages of 0.025, 0.06, 0.09, 0.12, 0.16, 0.19, and 0.23 ML. The amount of oxygen desorbing at 160 K clearly depends non-linearly on the initial total $O_{2(a)}$ coverage (see also Fig. 3); molecular desorption is quenched at low initial O_2 coverages. The inset shows the fit of the kinetic parameters for an initial dioxygen coverage of 0.23 ML $O_{2(a)}$.

The desorption peak for dioxygen near 160 K shifts to lower temperature as the initial coverage increases, ranging between 171 K at the lowest coverage to 160 K at the highest attained coverage; the peak is asymmetric around its maximum (Fig. 2). The onset of desorption begins at 160 K for the lowest coverages and at 140 K for the highest coverages of dioxygen.

Figure 3: Relative fractions of dioxygen molecular desorption (160 K) and associative desorption (580 K) as a function of initial dioxygen coverage at 125 K (circles). At low coverages of dioxygen only associative desorption occurs due to the complete dominance of dissociation at 160 K. At 0.18 ML the probabilities of the two channels intersect, and at the highest coverages molecular desorption accounts for the higher fraction of the two channels. The data point obtained at 0.29 ML O_{2(a)} was obtained for a 90 K exposure; the intensity of the 160 K state was determined using peak-fitting software to subtract non-dissociative 120 K state. The diamonds were obtained from calculated branching ratios (see Discussion). The dashed lines are only a guide to the eye to illustrate the trends.

Prior studies suggest that thermal- and photo-dissociation of molecular oxygen at 160 K drives the molecular desorption.[16,19-21] Accordingly, using areas of the temperature programmed desorption peaks, the relative amounts of oxygen that desorb from the molecular desorption channel (160 K) and the recombination channel (580 K) can be expressed as a branching ratio, defined as the ratio of dioxygen desorbing molecularly to the sum of the dioxygen desorbing at both 160 K and 580 K. Notably, the distribution of desorption between the two states exhibits a strong dependency on the initial dioxygen coverage (Fig. 3). Dissociation is

the exclusive reaction channel observed at coverages below 0.05 ML $O_{(a)}$ (0.025 ML $O_{2(a)}$) and remains the dominant channel at oxygen coverages below 0.35 ML $O_{(a)}$ (0.17 ML $O_{2(a)}$). At coverages above 0.35 ML $O_{(a)}$, molecular desorption is the primary pathway.

Figure 4: Top: Temperature-programmed desorption spectra of the recombination of dioxygen as a function of increasing oxygen coverage. As coverage is increased, the peaks narrow in width and shift to higher temperatures. Bottom: Simulated temperature-programmed desorption spectra of the same process using parameters obtained from the isothermal fitting analysis (see discussion). The coverage was varied between 0.05 ML $O_{(a)}$ and 0.50 ML $O_{(a)}$; in these experiments O_2 was dosed at 300K (see also Fig. S4 in the supplemental information).

As reported previously, the temperature programmed desorption peak for recombination of atomically adsorbed oxygen exhibits an increase in temperature and a peak-narrowing as the initial coverage of adsorbed oxygen increases (Fig. 4).[5,22] This behavior is certainly not typical

of second order recombination kinetics, and is indicative of a more complex coverage-dependence for the kinetics of recombination. In view of this behavior, a series of isothermal desorption experiments were performed for the saturation coverage of 0.50 ML $O_{(a)}$ (Fig. 5). For recombination kinetics exhibiting a simple kinetic order, the reaction rate would initially spike as the temperature is ramped up to a steady value and then decrease monotonically to zero as recombination proceeds. Instead, the isothermal desorption rate remains nearly constant initially and then *increases* at a coverage of 0.30 ML $O_{(a)}$. The rate continues to increase until 0.15 ML $O_{(a)}$ of oxygen remains, at which point the reaction rate decreases rapidly to zero.

Figure 5: Representative plots of the isothermal desorption rate of oxygen as a function of instantaneous oxygen coverage commencing with a coverage of 0.50 ML $O_{(a)}$. Temperature is plotted on the right axis. The recombination rate spikes initially due to temperature overshoot, which rapidly stabilizes. The rate behavior is indicative of an autocatalytic reaction. The data were fitted (solid line) to a model invoking the fragmentation probability of AgO chains. (see Discussion).

Discussion:

The two low temperature desorption states at 120 K and 160 K (Fig.1) correspond to differently oriented O₂ molecules within the troughs of the Ag(110) surface: at $T \leq 100$ K dioxygen adsorbs within the troughs of the Ag(110) surface oriented both along the $[1\bar{1}0]$ direction and the $[001]$ direction.[18] The O₂ $[1\bar{1}0]$ species, for which the molecular axis is aligned along the close-packed direction of the top-most silver atoms, is the only species which dissociates thermally and gives rise to the peak at 160 K.[18] The 120 K peak is associated with desorption of the species oriented along $[001]$. There is a significant discrepancy between the peak temperatures reported in this study and in previous work,[18] for which the temperature was calibrated for temperatures far below 100 K to discern physisorbed states.

The relative reaction fractions for molecular desorption and O₂ dissociation provide fundamental insight into the interplay between these competing events at 160 K. As noted above, the relative reaction fractions in Fig. 3 show a strong dependency on the initial coverage by chemisorbed O₂; at the lowest coverages there is exclusively dissociation; molecular desorption is observed only as the coverage increases. A ratio between molecular desorption (160 K) and dissociation (quantified by recombination at 580 K) of nearly 2:1 was observed following the saturation of the molecular state at 90 K at 0.3 ML (Fig. 3). This value is *significantly* higher than reported previously,[5,16] apparently because the adsorption temperature in the previous work was not sufficiently low to saturate the molecular desorption state at 160 K and because clean-off reactions by background gases may have interfered with the measurement.

O₂ dissociation and desorption at 160K show a strong non-linear coverage dependence: for low O₂ coverages dissociation is highly favored over desorption. In accordance with literature,

we propose that the interaction between migrating, “hot,” metastable oxygen adatoms prior to their equilibration with the surface and the chemisorbed dioxygen molecules causes the displacement of chemisorbed dioxygen, according to the following reaction scheme:

where the asterisk denotes a thermally-excited species. The invocation of mobile, unequilibrated, hot adatoms in thermally activated reaction mechanisms on metal surfaces has precedence in the literature.[23,24] The relative amounts of molecular desorption and adatom recombination reflect the encounter rate between hot oxygen adatoms and chemisorbed dioxygen; molecular desorption is concurrent with the dissociation of dioxygen. The strong coverage dependence of the branching ratio results from changes in the local packing density of the chemisorbed dioxygen prior to dissociation at 160 K, i.e., the changing probability of a hot adatom encountering an adsorbed molecule before the atom equilibrates with the surface. Further, were molecular desorption and dissociation to proceed independently with separate and distinct rate constants, molecular desorption would be expected at all coverages. *None* is observed at the lowest initial coverages of dioxygen studied here. Also, direct desorption of molecular oxygen with a peak at 160 K would indicate a binding energy of approximately 40 kJ/mol, far below the binding energy suggested for chemisorbed dioxygen of 75 kJ/mol.[25]

The competing rates between adsorption and dissociation can be understood in more detail from existing molecular understanding of chemisorbed dioxygen on Ag(110). As noted above, the chemisorbed dioxygen associatively adsorbs within the troughs of the (110) crystal face with

the molecular bond axis oriented in the $[1\bar{1}0]$ direction [11,18]. Upon dissociation, the dioxygen molecule yields two kinetically hot oxygen (i.e. thermally non-equilibrated) adatoms which migrate away from the point of origin. These oxygen adatoms migrate across the surface and relax by energy loss. During this process interactions with neighboring adsorbed dioxygen molecules may occur; displacement of chemisorbed dioxygen occurs, and the oxygen adatom thermalizes. Isotopic TPD studies, in which $^{18}\text{O}_2$ and $^{16}\text{O}_2$ are co-dosed, demonstrate the absence of isotope exchange in the collision-induced molecular desorption.[5] It follows that the interaction of the oxygen adatom with dioxygen does not activate any additional chemical channels beyond desorption. The density of chemisorbed dioxygen on the surface dictates the frequency of the hot oxygen atom encounters with dioxygen.

Kinetic rate equations for reactions 10-12 (above) provide the following relations, assuming the steady-state approximation for $\text{O}_{(a)}^*$:

$$\frac{d[\text{O}_{(a)}^*]}{dt} = 0 = 2K_1[\text{O}_{2(a)}] - K_2[\text{O}_{(a)}^*][\text{O}_{2(a)}] - K_3[\text{O}_{(a)}^*]; \quad (13)$$

$$\Rightarrow [\text{O}_{(a)}^*] = \frac{2K_1[\text{O}_{2(a)}]}{K_2[\text{O}_{2(a)}] + K_3}$$

$$\frac{d[\text{O}_{2(g)}]}{dt} = \frac{2K_2K_1[\text{O}_{2(a)}]^2}{K_2[\text{O}_{2(a)}] + K_3} \quad (14)$$

$$\frac{d[\text{O}_{2(a)}]}{dt} = -K_1[\text{O}_{2(a)}] - \frac{2K_2K_1[\text{O}_{2(a)}]^2}{K_2[\text{O}_{2(a)}] + K_3} \quad (15)$$

$$\frac{d[\text{O}_{(a)}]}{dt} = 2K_1[\text{O}_{2(a)}] = 2R_{diss} \quad (16)$$

The probability that a migrating oxygen adatom O^* reaches an adsorbed O_2 before it equilibrates with the surface can be approximated as being proportional to $\exp(-\frac{d}{\lambda})$, where d is the mean distance to the chemisorbed O_2 molecule and λ is the mean free distance traveled by the oxygen adatom prior to thermalization relative to a neighboring dioxygen (for an explanation of the exponential dependency see supplemental information). This relationship expresses the probability that the thermally hot adatom encounters a chemisorbed dioxygen before the adatom equilibrates with the surface. Accordingly, one can substitute the rate of adatom- O_2 encounters as $K_2[O_{2(a)}] \sim \exp(-\frac{d}{\lambda})$. It follows that the probability that an $O^*_{(a)}$ does *not* encounter a chemisorbed dioxygen and thus cannot cause molecular desorption can be approximated with $(K_3) \sim 1 - \exp(-\frac{d}{\lambda})$. After the additional substitution of $K_1[O_{2(a)}]$ with R_{diss} in Eqn. 14 and introduction of the heating rate $\beta = dT/dt$ this leads to:

$$\frac{d[O_{(a)}]}{dT} = \frac{R_{diss}}{\beta} = \frac{\nu_{diss}}{\beta} [O_{2(a)}] \exp\left(\frac{-E_{diss}}{RT}\right) \quad (17)$$

$$\begin{aligned} \frac{d[O_{2(g)}]}{dT} &= 2 \frac{R_{diss}}{\beta} \frac{K_2[O_{2(a)}]}{K_2[O_{2(a)}] + K_3} = 2 \frac{R_{diss}}{\beta} \exp\left(-\frac{d}{\lambda}\right) \\ &= 2 \frac{\nu_{diss}}{\beta} [O_{2(a)}] \exp\left(\frac{-E_{diss}}{RT}\right) \exp\left(-\frac{d}{\lambda}\right) \end{aligned} \quad (18)$$

where β denotes the sample heating rate during a TPD experiment. Eqn. 17 describes the dissociation rate (not directly observable) and Eqn. 18 quantifies the desorption rate (observable

as the peak at 160 K). The desorption rate shows the same temperature dependency and prefactor as the dissociation rate; apart from the factor $2 \exp(-\frac{d}{\lambda})$ both rates are identical.

A self-consistent analysis of the shape of the molecular desorption peak, the coverage dependency of the desorption peak temperature (Fig. 2) and the branching ratio for molecular desorption *vs* dissociation (Fig. 3) yields a mean free path of 1.8 nm. Desorption and dissociation rates during a TPD experiment were calculated from Equations 17 and 18, self-consistently computing d and λ . For example, $\lambda = 0$ would correspond to a branching ratio equal to zero (no low temperature molecular desorption), while $\lambda = \infty$ would lead to branching ratio of 0.66 (the two oxygen adatoms resulting from *one* dissociation event would always find *two* oxygen molecules). As a first step of the analysis the desorption peak for an initial coverage of 0.46 ML O_(a) (0.23 ML O_{2(a)}) was fitted (see inset in Fig. 2); the O₂-O₂ distance d was estimated by $d = a / (\Theta_{\text{initial}} - D_{\text{O}_2}) = ((2.89 / 0.23) - 3) \text{ \AA}$, where a is the surface lattice constant in $[1\bar{1}0]$ direction, Θ_{initial} is the initial O₂ coverage, D_{O_2} is the length of O₂ molecules. This geometric approximation assumes an even distribution of the dioxygen molecules. D_{O_2} was estimated as approximately twice the bond length of an O-O single bond in peroxides. Apart from reproducing the peak shape for the 0.23 ML desorption feature (condition (I)), the complete analysis must (II) reproduce the branching ratio (Fig. 3) for all initial coverages studied, and (III) account for the observed coverage dependent peak-temperature shift and peak asymmetry (Fig 2). Fitting the second and third conditions required a constant effective distance, d , between adjacent O₂ molecules that agreed well with $a / \Theta_{\text{initial}} - D_{\text{O}_2}$ (Fig. 6) throughout the course of desorption. A more complex analysis, in which the average distance between adsorbed dioxygen molecules was allowed to vary during the desorption process according to $d = a / \Theta - D_{\text{O}_2}$ (with d increasing during the process as Θ decreases), did *not* yield correspondence with experiment. This result

suggests that as O_2 dissociates oxygen adatoms accumulate on the surface and hinder redistribution of the remaining chemisorbed O_2 , presumably by blocking O_2 migration in the channels (see supplemental figure S2). This appears to be a reasonable hypothesis, as it is known that the O adatoms compete with dioxygen for fourfold hollow sites in the troughs,[11] and that such strongly bound species can produce one dimensional confinement of more mobile, diffusing species.[26]

Decrease of peak temperature with increasing coverage, peak shape and branching ratios where well reproduced by the model. The analysis yielded a value for λ of 1.8 nm, an activation energy of ~20 kJ/mol, and a frequency factor ν_{diss} of $\sim 6 \times 10^5 \text{ s}^{-1}$, the latter two values in good agreement to the results obtained by heating rate variation [5]. The origin of the magnitude of these values is not understood at this time.

The kinetic equations predict that the branching ratio is given by:

$$I_{\text{Des.}}/(I_{\text{Des.}} + I_{\text{Diss.}}) \sim K_2[O_{2(a)}]/(K_2[O_{2(a)}] + K_3) = \exp\left(\frac{-d}{\lambda}\right) \quad (19)$$

which is indeed observed (Fig. 7).

Figure 6: O_2-O_2 distances calculated from a comparison of the molecular dimension of O_2 and the Ag(110) lattice constant in $[1\bar{1}0]$ direction (filled circles) and simulated (self-consistent analysis – open circles) are overlaid and correspond well. Schematic: a depiction of a probable chemisorption configuration of the saturated $[1\bar{1}0]-O_2$ species.

Figure 7: Exponential dependency of the relative reaction fraction of desorption to the effective O₂-O₂ distance. The dashed line is a fit to $\exp(-d/\lambda)$ according to the approximation in Eq. 19.

The values obtained for the mean free path and the value of d (the O₂-O₂ distance) in the high coverage limit agree with previous studies, lending confidence in the analysis of the kinetics reported here. The value for λ of 1.8 nm is similar to that obtained with molecular dynamics simulations, which indicate that oxygen atoms migrate to distances between 0.5 and 2.2 nm within the first 10 ps after dissociation if they have an initial translational energy between 1 and 2 eV.[20] Though details of the transition state energy for the dissociation process are not known, the overall exothermicity of process can be estimated from the difference between the binding energy of the peroxide molecule (75 kJ/mol [25] i.e. ~0.4 eV per O atom) and the binding energy of the oxygen adatoms on Ag surfaces which has been estimated to be 3 eV.[27] Thus initial

kinetic energies exceeding 1 eV are not unreasonable. This detail awaits clarification by dynamical simulations of the dissociation process. Similar to thermal dissociation, photodissociation of chemisorbed O₂ also results in a relative branching ratio for desorption of 0.66 in the high-coverage limit.[21] The authors conclude that molecular dissociation and desorption channels accessed through photochemical means are likely the same channels responsible for thermal dissociation chemistry. The good agreement between the O₂-O₂ distance obtained by the self-consistent analysis and the estimation $d=a/\Theta_{\text{initial}}-D_{\text{O}_2}$ (Fig.6) strongly suggests that O₂ molecules are mobile in the temperature range of desorption, essentially behaving like a one-dimensional gas (which is, however, increasingly confined by oxygen adatoms during the dissociation/desorption process, see Fig. S2). This is in line with STM experiments demonstrating that O₂ is immobilized at 80 K and below where, at all oxygen coverages studied, the oxygen molecules condensed into one-dimensional islands with an O₂-O₂ distance of 2.89 Å [28,29].

The isothermal desorption spectra exhibit an increase in the rate of recombination as the reaction proceeds. Such autocatalytic behavior, “explosive” surface metal-oxide decomposition, has been described previously for platinum, palladium, gold, and other metals.[30-33] On Pt(111)-O_(a) and Pd(111)-O_(a) it is believed that large oxide islands decompose, providing O_(a) to a diffuse phase from which it subsequently recombines and desorbs, recombination being the rate-limiting process. In this island-disperse mechanism, the rate of recombination is posited to be proportional to the surface area of the dilute phase, which increases as the decomposition of the islands progresses.[30,31] On Ag(111)-O-p(4x4), island morphology is demonstrated to play a major role in kinetics of oxygen recombination.[34] Similarly, site-creating autocatalysis mechanisms have also been advanced to successfully explain the autocatalytic decomposition of

adsorbed carboxylates; the rate of reaction being proportional to the product of the surface coverage with the number of available sites, or $\Theta(1-\Theta)$. [35-37] Coverage dependent activation energies have also been invoked to explain this type of reaction. [38]

The autocatalytic reaction observed here appears to be the consequence of the evolution of the structure of the surface-reconstructed oxygen overlayer as desorption proceeds. It is well known that the chain-like structure of adsorbed $O\{AgO\}_m$ fragments progressively as the coverage of oxygen adatoms decreases. [39] Prior studies of CO oxidation on Ag(110)-O_(a) report a mechanism which is analogous to the explanation of the recombinative oxidation of O_(a) advanced in this work. [39] On Ag(110) repulsive interactions between the added rows of the $O\{AgO\}_m$ reconstruction inhibit segmentation of the individual $O\{AgO\}_m$ chains. Between 250 – 300 K segments form within the [001]-oriented $O\{AgO\}_m$ rows and oscillate in the $[1\bar{1}0]$ direction. These displaced chain segments result in low-coordinated terminal oxygen atoms which are reactive with CO. The amplitude of the oscillation and number of fragments is dependent on the surface temperature and the overall density of $O\{AgO\}_m$ chains, increasing as temperature increases and the coverage of O adatoms decreases. Similar to this mechanism, the unreconstructed Cu(110)-O was found to be very reactive for CO oxidation, while the (2x1) reconstructed surface severely inhibited the reaction rate. [40]

Both the isothermal desorption and temperature programmed desorption of oxygen above 520 K can be explained by this fragmentation of the added row structure. As the reaction proceeds and the surface coverage of chains decreases continuously, increasingly fragmented chain structures form, exposing increasing numbers of chain terminating oxygen adatoms, which are reactive.

The increase in the AgO chain fragmentation probability with decreasing oxygen coverage can be quantified *empirically* by Equation 20 where it is assumed that the degree of fragmentation increases exponentially with decreasing coverage. The corresponding parameters in this expression were obtained self-consistently by reproducing (i) the TPD spectra in Fig. 4, (ii) the isothermal desorption curves in Fig. 5, and (iii) the number of fragments per AgO chain as observed by Nakagoe et al. with STM. Using only one exponential function during the following analysis was not sufficient to reproduce the isothermal and TPD data; the segments appear to fragment more rapidly as the coverage becomes very low. Basically, the equation can be interpreted as the factor by which the fragmentation probability, and thus the number of reactive AgO chain ends, increases with decreasing coverage compared to the chains observed in the (2x1) saturation coverage.

$$N_{seg.}(\theta) \propto 1 + b \exp\left(c \frac{0.5 - \theta}{0.5}\right) + d \exp\left(e \frac{0.5 - \theta}{0.5}\right) \quad (20)$$

The rate of oxygen adatom recombination can be reproduced by assuming an equilibrium between the number of oxygen adatoms and the number of $O\{AgO\}_m$ chain fragments. The rate of oxygen adatom recombination can be modeled assuming a dilute phase of $O_{(a)}$ in equilibrium with the ‘condensed’ $O\{AgO\}_m$ chains, the concentration of O adatoms ($\Theta_{O(a)}$) in the dilute phase being proportional to the total O coverage (θ) times the number of segments per chain (given by Eq. 20). Thus, assuming second order kinetics for recombination of the oxygen adatoms in this dilute phase, one obtains:

$$\begin{aligned} d[O_2]/dt &= v \left(\frac{\Theta_{O(a)}}{0.5}\right)^2 \exp\left(\frac{-E_{rxn}}{RT}\right) \\ &= v \left(\frac{\theta}{0.5}\right)^2 \exp\left(\frac{-E_{rxn}}{RT}\right) \left(1 + b \exp\left(c \frac{0.5 - \theta}{0.5}\right) + d \exp\left(e \frac{0.5 - \theta}{0.5}\right)\right)^2 \end{aligned} \quad (21)$$

E_{rxn} includes the activation energy for the recombination step and the energy required for the chain fragmentation. Note that all coverages have been normalized to the saturation coverage of 0.5 ML. Eqn. 21 may be used to analyze both, the isothermal and TPD spectra.

A simultaneous fit of the isothermal desorption spectra and the TPD was used to extract prefactor ν , activation energy E_{rxn} , and the fragmentation parameters b to e in Eq. 21. The rate of oxygen adatom recombination is the product of coverage dependent and coverage independent terms. The coverage dependency of the factor $\theta^2 \left(1 + b \exp \left(c \frac{0.5-\theta}{0.5} \right) + d \exp \left(e \frac{0.5-\theta}{0.5} \right) \right)^2$ in Eq. 21 describes the variation of the desorption rate as a function of θ and in particular the local maximum of the desorption rate at ~ 0.15 ML (Fig.5). The fragmentation parameters b to e may be obtained by a fit of the isothermal data to Eqn. 21, or alternatively by directly fitting Eqn. 20 to the isothermal data after their normalization to θ^2 (see also Fig. S3 in the supplemental information); in both cases the coverage independent portion, $\nu \exp \left(\frac{-E_{\text{rxn}}}{RT} \right)$, appears only as a prefactor. Subsequently, the values of ν and E_{rxn} may be extracted by an analysis of the TPD data in Figure 4. However, instead of treating isothermal and TPD data separately, a simultaneous optimization of the parameters in Eqn. 21 to the isothermal *and* TPD spectra was performed and resulted in the following parameters: $\nu = 1.04 \times 10^{14} \text{ ML}^{-1} \text{ s}^{-1}$, $E_{\text{rxn}} = 171.4 \text{ kJ/mol}$, $b = 3.4 \times 10^{-12}$, $c = 28.6$, $d = 9.2 \times 10^{-2}$, and $e = 4.6$. In addition to the exponential growth proportional to $\exp(4.6(0.5-\theta)/0.5)$ the fragmentation increases drastically as soon as the coverage falls below ~ 0.1 ML where $\exp(28.6(0.5-\theta)/0.5)$ becomes dominant. The TPD and isothermal curves which correspond to these parameters are displayed in Fig.4 and Fig. 5. The calculated TPD curves show the transition from a symmetric to a more asymmetric peak shape and a correct up-shift of

the peak temperature with increasing coverage; furthermore the calculations also reproduce the intersections of different TPD traces. However, the calculated peak FWHM is systematically by ~ 6 K smaller than the experimental spectra (Fig. S4 in the supplemental information). This may be due to sample inhomogeneities which are not accounted for in the model and pumping speed limitations in the TPD apparatus. For further comparison of the results, leading edge analysis by Bowker et al. showed an activation energy of 173 kJ/mol, while heating rate variation (Figure S5) yields 163 kJ/mol; both of which compare well to this analysis [14].

An analysis of prior STM work on chain fragmentation confirms that Eqn. 21 describes the dependency between fragmentation probability and oxygen coverage well. Nakagoe et al. provide fragmentation fractions for two (nx1) $O(AgO)_m$ reconstructions as a function of temperature [39]. Normalization of the number of fragments observed in a (5x1) and (9x1) O/Ag(110) structure with the factor $\left(1 + 3.43 \times 10^{-12} \exp\left(28.61 \frac{0.5-\theta}{0.5}\right) + 0.0923 \exp\left(4.63 \frac{0.5-\theta}{0.5}\right)\right)$ – as obtained from the fit to the isothermal and TPD data – leads to a complete overlap of both curves (compare Fig. 4 in the work of Nakagoe et al. [39] and Fig. 8 in this work). Apart from the increase of fragmentation with decreasing coverage, a temperature increase clearly causes an increase in fragmentation. Assuming a temperature dependence of the form $\exp\left(-\frac{E_{frag}}{RT}\right)$, a fit of the normalized curves in Fig. 8 results in a value for the fragmentation energy of ~ 25 kJ/mol.

Figure 8: Least-squares fit of fragmentation frequency as a function of temperature for the Ag(5x1)-O and Ag(9x1)-O surfaces. Fragment counts were normalized to $\left(1 + 3.43 \times 10^{-12} \exp\left(28.61 \frac{0.5-\theta}{0.5}\right) + 0.0923 \exp\left(4.63 \frac{0.5-\theta}{0.5}\right)\right)$ prior to fit. From the temperature dependence, the activation energy for segmentation was determined to be 25 kJ/mol.

Coupling the temperature and coverage dependence of the chain fragmentation with the kinetic analysis affords an understanding of the mechanisms of oxygen recombination. At low coverages the peak shape is symmetrical around the maximum, indicating a second order process; however, with increasing coverage the peak temperature increases, opposite to the expected normal second order kinetic behavior, and the peak shape is increasingly asymmetric. Asymmetric peak shapes and a peak temperature increase typically indicate a zero order process, however, the leading edges of the high and low-coverage peaks do not lie on top of each other as would be expected. The fragmentation behavior explains this effect in the following way. At low

coverages fragmentation is significant even at temperatures far below the recombination temperature, and given that the number of free oxygen adatoms is proportional to the density of $O(AgO)_m$ chain ends, it follows that the surface is relatively rich in free oxygen adatoms. The rate-limiting step for O_2 desorption is the encounter of two oxygen adatoms and their recombination. Thus the peak exhibits the characteristic shape of a second order process. However, at higher coverages fragmentation is much less pronounced. Although the recombination process still requires two oxygen adatoms, their number is limited by the number of chain ends. Therefore, the creation of chain ends becomes effectively the rate limiting step. Furthermore, as the surface oxygen concentration approaches saturation, creation of fragments becomes increasingly difficult. As a consequence, the shift in the leading edge of the recombination peaks to higher temperature reflects decreasing fragmentation for higher coverages at a given temperature. The simulated and measured spectra clearly show the transition from a symmetric second order (characteristic for low coverages) to a more asymmetric peak shape.

Conclusions:

Chemisorbed dioxygen dissociates on Ag(110) near 160 K. Dissociation produces thermally hot oxygen adatoms which, in turn, displace chemisorbed dioxygen. The efficacy of this displacement process increases with increasing initial coverage of dioxygen. Measurement of the fraction of molecular species displaced as a function of the initial dioxygen coverage provides a value of the relative mean free path of the hot oxygen adatoms of approximately 1.8nm. Two oxygen molecules are displaced by every dissociation event if the neighboring dioxygen molecules are within a distance of 0.58 nm, or about 2 lattice units.

Lateral interactions within and between the reconstructed $O(\text{AgO})_m$ chains comprising the oxygen adatom surface phase explain the unusual recombination kinetics of adsorbed oxygen atoms. Reactive oxygen adatoms are provided by terminal sites in the $O(\text{AgO})_m$ chains, and their number depends sensitively on both temperature and the surface coverage of atomic oxygen, increasing as the oxygen coverage decreases and the temperature increases. This characteristic produces an isothermal acceleration in the rate of recombination as the coverage of oxygen adatoms decreases and causes a transition from second order to more complex kinetics in with increasing initial coverage of adsorbed oxygen temperature programmed desorption.

Acknowledgements: We gratefully acknowledge the support of the US Department of Energy, Office of Basic Energy Sciences, Catalysis Science Program under grant number DE-FG02-84-ER13289. RJM also gratefully acknowledges the support of the National Science Foundation, Division of Chemistry, Analytical and Surface Science CHE-0952790. MS acknowledges the generous support of the Alexander von Humboldt Foundation through Feodor Lynen Fellowship.

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