Establishing the LaMnO₃ Surface Phase Diagram in an Oxygen Environment: An ab Initio Kinetic Monte Carlo Simulation Study

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Supporting Information

ABSTRACT: We employ first principles methods to simulate the steady-state catalytic interaction of oxygen with the LaMnO₃(001) surface under varying levels of oxidative environment. First, density-functional theory together with transition-state theory is used to obtain the energetics and activation barriers of the relevant elementary surface chemical processes. The results were subsequently fed into a kinetic Monte Carlo (kMC) simulation scheme to explicitly account for the correlations, fluctuations, and spatial distributions of the oxygen adatoms and ad-molecules at the surface of the catalyst under steady-state conditions. Adsorbate—adsorbate lateral interactions and influence of the local environment on the reaction kinetics were adequately taken into account to compute (p, T) surface phase diagrams under equilibrium and metastable situations. The kMC-based approach allows



us to describe the kinetics-related effects such as the influence of the thermochemical history of the sample on the metastable regions of the (p, T) surface phase diagram. Features of the computed metastable phase diagrams are in excellent correspondence with available temperature-programmed desorption and catalysis experiments.

I. INTRODUCTION

Perovskite oxide surfaces catalyze many important oxidation reactions such as hydrocarbon combustion, carbon monoxide oxidation, oxidative dehydrogenation of alcohols, and the oxidative coupling of methane to form C_2 hydrocarbons.^{1–7} More recently, they are under active investigation for their potential use as oxygen ion conducting cathode materials in solid oxide fuel cells (SOFCs) and efficient catalytic devices for deNO_x processes in autoexhaust aftertreatment.^{8,9} In all the above applications, O chemistry at the perovskite surfaces is of central importance.

Among the perovskite oxides, LaMnO₃ has recently been shown to be superior to the conventional Pt-based catalysts for NO oxidation in diesel autoexhausts.¹⁰ An important feature of LaMnO₃ and many related perovskites is their ability to reversibly absorb and desorb oxygen into the crystal lattice by continuous and spontaneous changes in Mn oxidation state, without changing the overall bulk crystal structure. Therefore, the relevant processes including oxygen adsorption, desorption, dissociation, and surface diffusion on these systems have been targeted by many experimental studies.^{11–17} However, the difficulties associated with distinguishing between surfaceadsorbed and lattice oxygen have significantly limited the insights from the experimental data. Furthermore, identifying the catalytically active sites and acquiring a mechanistic understanding of surface chemical reactions are quite difficult based on experimental studies alone, mainly due to the lack of in situ experimental techniques which can provide atomically resolved details of the catalyst at high pressures.

Numerous first principles studies based purely on density functional theory $(DFT)^{18-20}$ have aimed at clarifying the atomic and electronic structure of LaMnO₃,²¹⁻²⁵ as well as at an understanding of O interaction with La MnO_3 .^{26–29} The MnO₂-terminated (001) surface of LaMnO₃ has been identified as the most stable surface facet at high temperature and high O partial pressure.²⁶ The adsorption and dissociation of oxygen on LaMnO₃ surfaces have been studied on this and other surfaces as well,²⁷⁻²⁹ leading to the conclusion that the dissociative adsorption of O2 is thermodynamically favored on LaMnO₃ surfaces (in contrast to that on the isostructural SrTiO₃ surfaces). All past studies are based purely on DFT and hence capture only the thermodynamics and the local kinetics (in terms of barriers to elementary steps). However, the actual surface chemistry and catalytic performance is dominated by factors such as larger scale kinetic hindrance, lateral interactions, and the thermal and environmental history that a sample has undergone. None of these factors can be practically handled using pure DFT calculations.

In the present study, our aim is to describe the thermodynamics, steady-state kinetics, metastability arising from sample history, and the long-time and large-length scale

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Received:August 23, 2012Revised:November 30, 2012Published:December 1, 2012
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Figure 1. Computed (p, T) surface phase diagrams for the MnO₂-terminated (001) LaMnO₃ surface exposed to an oxygen reservoir using (a) first principles thermodynamics as well as (b) equilibrium and (c) metastable surface phase diagrams using the kinetic Monte Carlo (kMC) approach. The top left corner of the three panels corresponds to O₂ condensation on the surface at very high oxygen chemical potentials. Isocoverage lines in panel a at the phase boundary between clean and 100% O covered regions represent a 25% increase of O ad-atoms, while the isocoverage lines panels b and c capture variations of ~12% surface coverage of O ad-atoms.

behavior of the MnO₂-terminated LaMnO₃ surface in contact with an oxygen reservoir, as a function of temperature (T) and partial pressure (p) of oxygen. The enormously successful first principles thermodynamics (FPT) approach³⁰⁻³⁵ that combines DFT results with statistical thermodynamics allows us to predict the equilibrium surface phase diagram of the MnO2terminated LaMnO₃ surface in a relatively straightforward manner. However, while the configurational entropic contributions can in principle be incorporated (although it may not be straightforward and computationally efficient), inaccessibility to the kinetic and history-dependent effects is a major limitation of the FPT approach. Fortunately, the kinetic Monte Carlo (kMC) scheme (employing parameters computed using DFT) offers a powerful strategy to properly describe the overall kinetics (including kinetic "hindrance") of a collection of coupled and competing elementary processes.³⁶ Moreover, the kMC approach also allows for the proper inclusion of the history that the system has undergone, such as cooling or heating schedules that accompany temperature-programmed desorption (TPD) or catalysis experiments.

The basic elements of the kMC strategy may be described as follows. The DFT-computed total energies of various oxygencovered surface configurations may be used to parametrize a lattice gas Hamiltonian (LGH). The LGH strategy provides an inexpensive and accurate prescription for computing the total energy of systems much larger than can be directly handled by modern DFT methods.^{37–48} Such an LGH scheme can be combined with transition-state theory49 (with barriers for elementary processes computed using DFT) and Monte Carlo methods to treat multiple processes simultaneously at large length and time scales. Here, such kMC simulations have been carried out at various values of T and p for the MnO2terminated (001) LaMnO₃ surface, where the time evolution has been efficiently coarse grained to the rare-event dynamics. Steady-state results obtained from the kMC simulations at different T and p values can be used to extract the surface phase diagram.

The kMC approach grants access to kinetics-related effects and history dependence which are not directly accessible using DFT or FPT. While thermodynamic equilibrium may dictate the presence of a certain surface configuration, the pathway that may lead to the realization of the surface configuration may be difficult to achieve. For instance, the presence of two O adatoms at adjacent surface sites (even if thermodynamically favored) will only happen if those two surface sites were vacant to begin with. The kinetic hindrance that results if one or both of those sites are unavailable for adsorption and the condition of the surface before exposure to oxygen or the rate at which T or p change (i.e., the "history") are naturally captured within kMC. Incorporation of such factors leads to metastable phase diagrams which are of practical relevance, e.g., in explaining features seen in TPD and catalysis experiments—situations in which a system is rarely at equilibrium with its surrounding environment.

Figure 1 contains the essence of our findings for the MnO₂terminated LaMnO₃ surface in contact with an oxygen reservoir. Figure 1a presents the (p, T) equilibrium surface phase diagram which is purely based on thermodynamic considerations (i.e., using the FPT approach), and Figure 1b shows the kMC result which attempts to replicate the FPT conditions. For the case in hand, we find that the dissociative adsorption of oxygen is energetically more favored as compared to the molecular adsorption. However, the dissociative adsorption is a slightly activated process while the molecular adsorption is barrierless. Therefore, at low temperatures a clean surface, when exposed to oxygen, is expected to undergo a spontaneous molecular adsorption. Attainment of the thermodynamic equilibrium state (viz., a 100% oxygen ad-atom covered surface) becomes possible only at temperatures high enough to supply sufficient thermal energy to overcome kinetic barriers for molecular desorption and surface dissociation. Therefore, for a clean surface a metastable surface phase diagram is of more practical relevance in the low-temperature regime while the equilibrium surface phase diagram is recovered at the high temperatures. Such a metastable (p, T)surface phase diagram calculated in the present study is shown in Figure 1c. We further note that the phase boundaries on the surface phase diagrams are expected to correlate with desorption (both molecular and associative) peaks of oxygen in TPD experiments and provide a direct pathway to compare our theoretical finding with experimental observations. The short and long red bars in Figure 1c indicate the observed molecular and associative oxygen desorption peak positions in the experiments.^{50,51} Our results show that the two equilibrium surface phase diagrams are unable to capture the observed molecular desorption peak while the metastable surface phase diagram (Figure 1c) is able to reproduce the experimental observations.

Figure 1 also enables us to understand and explain the experimentally observed catalytic behavior of LaMnO₃. Following the Sabatier principle, we note that phase boundaries on the surface phase diagrams are expected to correlate well with the high catalytic activity regimes on the pressure and temperature scales. The Sabatier principle, which is a fundamental concept in catalyst design, states that in a high catalytic activity regime the interaction between a surface catalyst and the reactant adsorbates should be neither too strong nor too weak. If the interaction is too weak, the reactants will fail to bind to the catalyst and no reaction will take place. On the other hand, if the interaction is too strong, the catalyst gets blocked by reactants or products that fail to dissociate. In the calculated equilibrium surface phase diagrams, the phase boundaries between clean and 100% O ad-atom covered surface regions represent the pressure and temperature conditions for such an optimum interaction. In fact, we note that the experimentally observed activity of the LaMnO₃ surface toward NO oxidation indeed shows a peak near the predicted phase boundary between clean and 100% O ad-atom covered surface regions on the equilibrium surface phase diagram.¹⁰ The above discussion clearly motivates the importance and necessity of kMC simulations in making connections with experimental observations in a high-fidelity manner.

The remainder of the paper is organized as follows. In section II, we describe technical aspects pertaining to our first principles calculations and models. Details concerning the kMC approach and LGH parametrization are provided in section III. Our results are discussed and compared with available experiments in section IV. Finally, we summarize our conclusions in section V.

II. TECHNICAL DETAILS

A. Computational Details. Our DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP),⁵² with core–valence electron interactions treated within the frozen-core projector augmented wave (PAW)^{53,54} approximation, and the GGA-Perdew-Wang-91 (PW91)55 exchange-correlation functional was used. The motivation behind using the PW91 functional in our study stemmed from the availability of relevant past works in the literature carried out mostly at the same level of theory.²⁵⁻²⁸ Plane-wave basis functions up to a kinetic energy cutoff of 400 eV were used, and the O 2s and 2p, the Mn 3p, 4s, 3d, and 6p, and the La 5s, 5p, 5d, and 6s electrons were included in the valence states. A 0.10 eV Gaussian smearing was applied to band occupancies near the Fermi level, and total energies were extrapolated back to 0 K. The structures were relaxed using a conjugate gradient algorithm until the forces on all atoms were <0.06 eV/Å. The spin-polarized method was used to properly describe the magnetic state of LaMnO₃ and the triplet ground state of oxygen. Sufficiently large grids were used to avoid socalled "wraparound" errors in fast Fourier transforms.

Activation barriers for various elementary surface reactions involving oxygen adsorption, desorption, surface dissociation, and surface diffusion were calculated using the nudged elastic band (NEB) method.^{56,57} Furthermore, we used normal mode vibrational frequency analysis to confirm that the identified saddle points indeed have a single imaginary vibrational frequency and are true transition states.

B. Model Details. LaMnO₃ is known to exhibit a ferromagnetic and three antiferromagnetic (A-type, C-type, and G-type)^{58,59} states. The A-type antiferromagnetic state is the experimentally observed low-temperature ground state of the system with the ferromagnetic state slightly higher in energy. However, at the high temperatures associated with the relevant technological applications (such as SOFC and catalytic convertors in autoexhausts), LaMnO₃ typically exhibits cubic symmetry, corresponding to the vanishing average Jahn–Teller distortion. In the present study, we have therefore performed calculations considering the prototypical high-temperature cubic perovskite structure with $Pm\overline{3}m$ symmetry.

The calculated bulk cubic lattice constant $a_0 = 3.89$ Å was found to be in good agreement with the corresponding experimental value of 3.95 Å, measured at 798 K.⁶⁰ The calculated cubic lattice constant was further used to construct cubic MnO₂-terminated supercell slab models containing seven layers and symmetric about the central mirror plane. The slabs were separated by 12 Å vacuum in the slab normal direction to minimize spurious unphysical interactions between periodic images. For each slab, the central three layers were kept fixed at the calculated bulk geometry and the top two and bottom two layers were allowed to relax. A $8 \times 8 \times 1$ Monkhorst-Pack *k*point mesh produced converged results for the (1×1) surface supercell, and the mesh was scaled appropriately for the larger (2×2) and (3×3) surface supercells.

In the present study, the total binding energy of N_0 oxygen ad-atoms and N_{O_2} oxygen ad-molecules on an LaMnO₃ surface was defined as

$$E_{b,N_{\rm O},N_{\rm O_2}}^{(n\times n)} = E_{N_{\rm O},N_{\rm O_2}}^{\rm DFT(n\times n)} - E_{\rm clean}^{\rm DFT(n\times n)} - \frac{1}{2}(N_{\rm O} + 2N_{\rm O_2})E_{\rm O_2}^{\rm DFT}$$
(1)

where $E_{N_0,N_{02}}^{(n \times n)}$ and $E_{clean}^{(n \times n)}$ represent the DFT energies of a $(n \times n)$ surface unit cell slab with the oxygen adsorbates (including oxygen ad-atoms and ad-molecules) and a clean $(n \times n)$ surface unit cell slab, respectively. The DFT energy of a single O_2 molecule (E_{O2}^{DFT}) was calculated by isolating the molecule in a 15 Å cubic cell in its spin-triplet ground state. A negative value of E_b indicates an exothermic nature of the oxygen adsorbate binding on the surface.

III. DETAILS OF THEORETICAL METHODS

In this section, we provide details of the first principles thermodynamics and kMC method used to compute the (p, T) surface phase diagrams of the LaMnO₃(001) surface. As the general computational methodology used here is well established and has been discussed in detail in the literature, ^{30–35,48,61–68} we keep our discussion brief. However, an interested reader is referred to a more detailed description provided in the Supporting Information.

A. First Principles Thermodynamics. To compare the thermodynamic stability of various adsorbed O and O_2 containing LaMnO₃(001) surfaces, we have calculated the surface energies of different surface configurations with varying amounts of atomic and molecular oxygen. However, we find that the dissociative adsorption of oxygen is always energetically preferred as compared to the molecular chemisorption, and only fully or partially oxygen ad-atom covered surface configurations are relevant from the thermodynamic stability point of view. Therefore, although we have considered a number of surface structures with varying configurations and a

range of surface coverages for molecular and mixed (i.e., with both O and O_2) adsorption, only selected configurations are depicted schematically in Figure 2. The surface free energy



Figure 2. O ad-atom and/or O_2 ad-molecule covered ordered surface structures that were used to compute FPT-based surface phase diagrams as well as the coverage-dependent binding energy and adsorbate–adsorbate lateral interactions for LGH fitting. O atoms are represented by small red spheres. Surface O ad-atoms and O_2 ad-molecules are indicated by pointing black (smaller) and blue (larger) arrows, respectively. Purple and green spheres represent surface Mn atoms and La atoms in the penultimate layer, respectively.

change $(\Delta \gamma)$ is determined relative to the clean surface and as a function of oxygen chemical potential according to

$$\Delta \gamma_{N_{\rm O},N_{\rm O_2}}^{(n\times n)}(p,\,T) = \frac{E_{\rm b,N_{\rm O},N_{\rm O_2}}^{(n\times n)} - \left(\frac{N_{\rm O}}{2} + N_{\rm O_2}\right) \Delta \mu_{\rm O_2}(p,\,T)}{n^2 A} \tag{2}$$

/ . .

where A is the surface area of a (1×1) surface unit cell and $\Delta \mu_{O_2}$ is the pressure- and temperature-dependent part of the oxygen chemical potential including the zero-point vibrational energy.⁶¹ As will be discussed in section IV.B, critical oxygen chemical potentials can be determined by plotting the $\Delta \gamma$ of the surface configurations against $\Delta \mu_{O_2}$, which eventually lead to the FPT-based (p, T) surface phase diagram.

B. First Principles Kinetic Monte Carlo Simulations. In this study, our aim is to describe the thermodynamics and steady-state kinetics of the surface in contact with an oxygen reservoir as a function of temperature and partial pressure of oxygen by explicitly accounting for the kinetics of the different elementary processes taking place in the system. Properly evaluating the time evolution of such a system at the atomic level requires simulation cells that are large enough to account for the effects of correlation and spatial distribution of various chemical species at the surface. Furthermore, most of the considered processes are activated and occur on time scales that are orders of magnitude longer than typical molecular/atomic vibrational time scales (10^{-12} s) . Due to these so-called rare events, we need to evaluate the statistical interplay between the different elementary processes over an extended time scale that can reach up to seconds or more. To achieve this goal, we employ kMC simulations, where the time evolution is efficiently coarse grained to the rare-event dynamics.^{69–73} Formally, the kMC algorithm provides an elegant and efficient way to solve the chemical master equation describing a system's evolution in terms of probability currents.⁷⁴ The master equation is given as

$$\frac{\mathrm{d}P_{\alpha}}{\mathrm{d}t} = \sum_{\beta(\neq\alpha)} \left(k_{\beta\to\alpha} P_{\beta} - k_{\alpha\to\beta} P_{\alpha} \right) \tag{3}$$

.

where P_{α} denotes the probability to find the system in a certain configuration α . $k_{\beta \to \alpha}$ is the rate constant of a reaction which leads the system to a final configuration α , starting from an initial configuration β . P_{α} is determined by the energy of the system in a configuration α , and $k_{\beta \to \alpha}$ is specified by the barrier for the β to α transformation. The essential ingredients to achieve a practical kMC scheme are thus (1) a prescription for computing the total energy of a given configuration and (2) a scheme to effectively compute the rates of all relevant possible elementary processes. These ingredients are described in the following paragraphs.

In order to rapidly calculate the total energy of several configurations (required for ensemble averaging) involving large supercells (required to properly account for spatial correlations), we have use DFT-parametrized two-dimensional LGH.^{37–48} The two- and three-body interactions between oxygen ad-atoms accounted for in the DFT-parametrized LGH include first-, second-, and third-nearest neighbor pair interactions as well as three different three-body interactions, namely, linear, triangular, and bent. To select the relevant terms to include in the expansion and to evaluate the accuracy of such an expansion, we use the leave-one-out (LOO) cross-validation (CV) method.⁷⁵ A detailed description of the LGH used and the LOO–CV method is provided in the Supporting Information.

Identification of all the relevant possible elementary processes and computation of their activation barriers is the second crucial ingredient of a kMC simulation recipe. The processes of interest in the present study include O₂ adsorption and desorption, O₂ surface dissociation and association, and O surface diffusion. Activation barriers calculated using NEB calculations for all these relevant elementary reactions are presented in Figure 3 and used to determine the $k_{\beta\to\alpha}$ rate constants (using transition-state theory) necessary for the kMC simulations as described in detail in the Supporting Information.

It is well-known that both the heat of reaction and the activation barrier of a given surface chemical reaction are affected by the presence of other neighboring adsorbate species.^{49,76–78} Since the activation barrier calculations are computationally intensive, it is a common practice to estimate the environment- and coverage-dependence of the barriers from just a knowledge of the heat of formation (or the energetics). In the present work, the dependence of the local lateral interactions on the activation barriers of the elementary



Figure 3. NEB-calculated minimum energy paths for oxygen (a) molecular adsorption, (b) dissociative adsorption, (c) surface dissociation, and (d) surface diffusion at Mn-on-top site for the (001) MnO_2 -terminated LaMnO₃ surface. For each of the four panels, initial and final states are also shown with red, green, and purple balls representing O, La, and Mn, respectively.

processes is accounted for by employing the Marcus equation,⁴⁹ as follows

$$E_{\rm a} = \left(1 + \frac{\Delta H_{\rm r}}{4E_{\rm a}^0}\right)^2 E_{\rm a}^0 \tag{4}$$

where $E_{\rm a}$ is the activation energy to be estimated and $\Delta H_{\rm r}$ is the heat of reaction (available from the LGH scheme). E_a^0 is a parameter which can be computed using $E_{\rm a}$ calculated for a limited number of configurations using eq 4. We note that the Marcus equation is a more general form of the frequently used Brønsted, Evans, and Polanyi $^{76-78}$ (BEP) relation which assumes a linear relationship between E_a and ΔH_r . The BEP relation has been shown to follow for many elementary surface reactions on different transition metal surfaces⁷⁹⁻⁸² and multicomponent surface systems such as Pt-Co and Pt-Fe⁸³ alloys. However, it is important to note here that the BEP relation works well only for reactions which are either moderately endothermic or exothermic. For instance, Figure 4 shows a comparison between the Marcus and BEP relation for the associative desorption of oxygen on the LaMnO₃ surface. It is clear that the Marcus equation and the BEP relation are in close agreement only for a narrow range of the ΔH_r . For large variations of ΔH_r , the BEP relation may lead to an unphysical situation of negative activation barrier while the activation barrier dictated by the Marcus relation is always positive.

Finally, we comment on the specific details pertaining to the kMC simulations. To compute the equilibrium surface phase diagram, a series of kMC simulations were performed at different T and p values of oxygen ranging from 100 to 1200 K and 10^{-10} to 10^{+6} atm, respectively. After each kMC step, the time is advanced according to⁷³

$$\Delta t = \frac{-\ln(\rho)}{K} \tag{5}$$

where *K* denotes the overall rate $K = \sum_{i=1}^{N_p} k_i$ of all N_p possible processes of the system and ρ is a random number between 0 and 1 (i.e., $\rho \in (0, 1]$). A (20 × 20) supercell (along the surface plane) with periodic boundary conditions was used in the present study. The convergence of our results was validated using a larger (30 × 30) cell for a small number of cases. Each simulation at a given *T* and *p* was allowed to equilibrate to a



Figure 4. Comparison between the Marcus and BEP relation for the variation in the activation barrier (E_a) as a function of the heat of reaction (ΔH_r) for the associative desorption of oxygen on the LaMnO₃ surface. The DFT-computed values of the E_a and the ΔH_r are also shown in parentheses.

steady state in which surface coverage of all the surface species reached constant values, with the obvious exception of small fluctuations resulting from the stochastic nature of the simulation.

IV. RESULTS AND DISCUSSION

A. Structure and Energetics of Oxygen Ad-Molecules on the (001) MnO_2 -Terminated LaMnO₃ Surface. Our previous study of atomic oxygen adsorption on the MnO_2 terminated (001) LaMnO₃ surface has shown that the Mn-ontop site is the only thermodynamically stable adsorption site out of the five different possible adsorption sites considered.²⁹ Similar conclusions have been drawn in a DFT study by Kotomin et al. for the low-temperature orthorhombic LaMnO₃(001) surface facets where they found that the dissociative adsorption of O₂ molecules from the gas phase is energetically favorable on the Mn surface ions even on a clean defect-free surface.²⁷ We note that such a behavior of LaMnO₃ surface is in contrast with other perovskite surfaces such as SrTiO₃⁸⁴ and PbTiO₃,²⁹ where adsorption of oxygen ad-atoms near the surface lattice oxygen leads to the formation of a molecular peroxide (O₂⁻²) species.

Along similar lines, in this section we discuss the energetics and structural details of the surface-adsorbed molecular oxygen. Chemisorption of O₂ molecule has been studied in detail on various transition metal surfaces and can generally be characterized as either superoxide (O_2^-) or peroxide (O_2^{-2}) depending on the extent of its reduction by the charge transfer from the metal. The more reduced peroxide species exhibits a frequency closer to 850 cm⁻¹ and bond lengths of 1.49 Å. On the other hand, the less reduced superoxide moiety typically exhibits vibrational frequencies near 1140 cm^{-1} and O-O bond lengths of 1.33 Å.⁸⁵ Furthermore, it is also well-known that an O₂ molecule can bind to a transition metal center in either mono- or bidentate modes. Therefore, here we have considered both the binding modes for the chemisorbed O_2 molecule on the surface transition metal on-top sites. However, as discussed below, the monodentate binding mode was found to be energetically more favored over the bidentate mode. Hence, the former was used in the LGH parametrization.

Figure 5 shows geometrical details of the DFT-optimized ground-state structure of an O_2 molecule adsorbed at the Mn-



Figure 5. Top and side views of DFT–GGA-calculated relaxed geometries of O_2 ad-molecules in monodentate (panels a and b, respectively) and bidentate (panels c and d, respectively) binding modes on the surface Mn-on-top site. Red, green, and purple spheres represent O, La, and Mn atoms, respectively.

on-top site. The monodentate O₂ binds in a bent fashion with Mn-O-O angle of around 121°, Mn-O bond length of 1.87 Å, and the O–O bond oriented along the [110] direction, i.e., along the diagonal of the surface unit cell. However, the surface-adsorbed molecule is relatively free to rotate around the surface normal with a negligible barrier of 0.02 eV for a 90° rotation. The chemisorption of the O2 molecule in the monodentate form was calculated to be exothermic with a surface binding energy of 0.77 eV with respect to the corresponding gaseous molecule. The O-O bond length was found to be 1.28 Å with the O-O stretching frequency of 1295.2 cm⁻¹, red-shifted by about 495 cm⁻¹ with respect to the molecular O₂. Bader charge analysis further indicates a charge transfer of 0.3 e⁻ from the surface to the near surface O atom of the adsorbed O₂ molecule. All these features are consistent with a superoxo-like O_2^- description of the adsorbed molecule.

On the other hand, the bidentate binding mode of the O₂ molecule on the Mn-on-top site at the surface was predicted to be energetically less favored by 0.24 eV as compared to the monodentate configuration. As shown in the Figure 5, the bidentate O2 molecule binds to the surface Mn ion almost horizontally with O-O bond length of 1.34 Å. A close inspection, however, reveals that the O-O bond axis is slightly tilted with respect to the horizontal, bringing one of the O atoms closer to the surface Mn ion by 0.01 Å. This asymmetry also shows up in the Bader analysis according to which a total of 0.57 e^- charge is transferred to the adsorbed O₂ molecule, 0.4 e⁻ of which lies on the near surface O atom. The bidentate binding mode of the O_2 molecule with an O–O stretching frequency of 1096.5 $\rm cm^{-1}$ is again in the regime expected for a superoxo-like molecular O2 species, though it shows a slightly more reduced nature through a decreased O-O stretching frequency and increased amount of Bader charges with respect to the monodentate binding mode.

B. Equilibrium Phase Diagram from First Principles Thermodynamics. As described in section III.A, by plotting the surface free energies of the surface configurations depicted in Figure 2 against $\Delta \mu_{O_2}$, we are able to find the most stable configuration for a given $\Delta \mu_{O_2}$, as well as the critical oxygen chemical potentials which correspond to a phase boundary on the (p, T) surface phase diagram. At this boundary, thermodynamic stability of the surface switches from one stable phase to another. Furthermore, it can clearly be seen from Figure 6 that the relative surface free energy for the



Figure 6. Plot of relative surface energy ($\Delta \gamma$, taken relative to the clean surface) as a function of oxygen chemical potential ($\Delta \mu_{O_2}$) for various O ad-atom and/or O₂ ad-molecule covered surface facets shown in Figure 2. The lower most envelop of the plot, representing the thermodynamically most stable surface facets at a given oxygen chemical potential, is highlighted. Critical oxygen chemical potentials are represented by yellow circles, and nomenclature of Figure 2 is used in labeling the lines.

oxygen ad-atom covered surface structures (shown in solid black lines) is always lower as compared to those with O_2 admolecules for any given oxygen chemical potential. This fact eliminates the appearance of any surface phases with molecular oxygen on the equilibrium surface phase diagram.

The resulting (p, T) equilibrium surface phase diagram computed using the FPT approach (i.e., derived from Figure 6 and the well-known T and p dependence of $\Delta \mu_{0,}$)^{32,33} is presented in Figure 1a. High temperature and low partial pressure in the lower right corner of the Figure 1a correspond to a very low chemical potential of oxygen (i.e., the concentration of the oxygen in the gas phase above the surface is insignificant), and consequently a clean $LaMnO_3(001)$ surface results as a stable system state. If we now move along the T axis toward the left and/or upward on the pressure axis in the Figure 1a, we reach more and more oxygen-rich conditions. The increase in the oxygen chemical potential leads to a stabilization of O ad-atom covered surface structures with increasing coverage: First, the 25% O ad-atoms covered surface shown in Figure 2b, then subsequently 50% and 75% O adatom covered surface structures (c.f., Figure 2c and e, respectively), and finally a monolayer of oxygen ad-atoms (i.e., a 100% O ad-atoms coverage) on the surface become the most energetically favored state of the system. Increasing the oxygen chemical potential even further (through unrealistically large partial pressure of oxygen and very low temperatures) finally leads to the formation of oxygen condensation onto the oxidized LaMnO₃(001) surface as indicated by the upper left region of the surface phase diagram.

We further note that the various transitions from one surface phase to other on the surface phase diagram generated within the FPT approach show up as abrupt transitions with sharp boundaries. However, under realistic conditions, one would

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rather expect a gradual increase in the O ad-atom population on the surface with coexistence of disordered regions. A rational explanation of the sharp phase boundaries can be traced back to the neglect of the configurational entropy to the free energy of the surface phases.³²

C. Equilibrium Phase Diagram from kMC Simulations. We now turn our discussion toward the surface phase diagram computed using the kMC approach, as described in section III.B and the Supporting Information. For the case in hand, at any given partial pressure of oxygen we start the simulation at 100 K with the 100% O ad-atom covered surface as a starting configuration. Once steady state is reached, the temperature is increased in steps of 10 K and the equilibrated surface from the immediate previous temperature was used as a starting configuration for the simulation at the next temperature. We further checked that the obtained phase diagram does not change if, for a given pressure, one starts with a clean LaMnO₃(001) surface at high temperature (1200 K) and then ramps down in temperature in a similar manner. The resulting steady-state kMC-simulated phase diagram is shown in Figure 1b and shows a good agreement with the FPT-generated phase diagram in Figure 1a. However, the kMC-simulated surface phase diagram in Figure 1b shows a slightly wider stability of partial O ad-atom covered regions. This difference can be attributed to several factors such as consideration of only a limited number of surface configurations in the FPT approach, finite size of the kMC surface unit cell with periodic boundary conditions, and proper incorporation of the configurational entropy in the kMC-based approach.

We note that, owing to the proper account of the surface configurational entropy in the kMC-based surface phase diagram, the transition from one surface coverage to the other on the phase boundary is not abrupt but gradually occurs over a finite range of pressures and temperatures. In fact, in the absence of lateral interactions the results of the kMC simulation at the phase boundary between clean and 100% O ad-atom covered surface are indeed identical to those resulting from the appropriate analytical expression for the Langmuir isotherm,⁴⁹ since the kMC algorithm automatically accounts for the configurational entropy.

D. Metastable Phase Diagrams. In the previous section, we presented a comparison between equilibrium surface phase diagrams generated using the FPT and kMC approaches. In generating the surface phase diagram based on the kMC approach, the starting surface configuration was deliberately chosen to be the thermodynamic ground state of the system at the starting point (i.e., O ad-atom covered surface in the temperature ramp-up run and a clean surface at high temperature in the temperature ramp-down run). Furthermore, an establishment of the equilibrium between the surface and the gas phase O_2 for each pressure and temperature condition during the course of the simulation was also practically possible. However, it might very well be that, due to the conditions maintained during the surface preparation, the starting surface configuration is very far removed from the equilibrium state of the system at that temperature and pressure. Furthermore, in such a situation, owing to the kinetic limitations an appropriate "realistic" pathway to the equilibrium state may not be accessible. For example, at low temperatures kinetics may be so slow that it becomes almost impractical to attain the groundstate surface configuration dictated by the thermodynamics. Behavior of such kinetically hindered systems can be captured using the concept of metastable surface phase diagram. In fact,

similar notions have recently been employed to explain the experimental observation of the (1×1) -H phase on Zn-terminated (0001) ZnO surface facets.⁸⁶ Below we discuss the determination of the metastable surface phase diagrams within the context of the oxygen interactions with the LaMnO₃(001) surface.

The examples of the metastable surface phase diagrams for the LaMnO₃(001) surface are shown in Figure 1c, which was generated by starting with a clean surface as the initial configuration at 100 K and equilibrating for 50 000 kMC steps. The temperature was then increased in steps of 10 K, and the final surface configuration from the previous temperature was used as a starting point for the next simulation. In starting up with a clean surface, each of the surface adsorption sites allows for either molecular or dissociative adsorption of oxygen as a possible elementary process. While the dissociative adsorption of an O_2 molecule has a small activation barrier of 0.05 eV, the molecular adsorption of oxygen (although thermodynamically less favored than the dissociative adsorption) is a barrierless process. At temperatures as low as 100 K a rather small activation barrier of 0.05 eV is sufficient to suppress the rate of the dissociative adsorption by 2 orders of magnitude relative to the unactivated molecular adsorption. As a result, the surface spontaneously favors a metastable state in which almost all of the surface sites are occupied with O₂ molecules.

A possible pathway to attain the thermodynamic ground state (i.e., a uniform monolayer coverage of O ad-atoms on the surface) is through desorption of an O_2 molecule followed by creation of a pair of O ad-atoms through the surface dissociation of another adsorbed molecule on a neighboring site. However, owing to an activation barrier of 0.93 eV for the surface dissociation, odds of the dissociation, against reoccupation of the vacant site by an another O2 molecule, are only 1 in 10³⁶ at 100 K. Furthermore, once the surface active sites have been consumed by O₂ adsorption at a starting low temperature (i.e., at 100 K), the molecular desorption is inhibited until the entropic contributions at the higher temperatures are large enough to overcome an activation barrier of 0.77 eV for the process. However, at higher temperatures, once the thermal energy at a given pressure becomes sufficiently large to drive the spontaneous molecular desorption of O_2 , the metastable surface phase diagram readily agrees with the thermodynamic phase diagram in Figure 1b. From the above discussion it is clear that while metastable situations may be inevitable at low temperatures, the equilibrium phase diagram is recovered at high temperatures when the thermal energy is sufficient to overcome the kinetic barriers. As will be discussed below, capturing such metastable situations at low temperatures is essential to achieve quantitative agreement with experiments such as TPD.

E. Comparison with Experiments. In the previous sections we have discussed the results of our kMC simulations aimed at investigating the state of a (001) MnO₂-terminated LaMnO₃ surface exposed to an oxidative environment at various temperature and pressure conditions, as dictated by thermodynamics and kinetic effects. In the present section we collect the relevant experimental data available in the literature to compare with the results of the kMC simulations.

Following our calculated surface phase diagrams, we expect both O_2 and O TPD peaks according to the metastable phase diagram in Figure 1c, but only the O peak as per Figure 1a or b. In an experimental kinetics study performed by Saracco et al.,⁵⁰ an LaMnO₃ surface was prepared by calcination at 800 °C. The

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temperature was then progressively lowered down to room temperature at a 3° min⁻¹ rate, thereby allowing complete oxygen adsorption on the catalyst surface. The excess oxygen molecules not chemisorbed on the surface were washed out by helium fed to the reactor at a 50 cm³ min⁻¹ flow rate. After 10 min at 25 °C, the temperature was raised to 900 °C at a 3 °C min⁻¹ rate. The variation of the outlet oxygen concentration as a function of temperature obtained by Saracco et al. shows a peak between 550 and 850 °C corresponding to the surface oxygen ad-atom desorption which is in excellent agreement with our surface phase diagram shown in Figure 1c (as well as with Figure 1a and b). Furthermore, we note that owing to the surface preparation at 800 °C and then slowly cooling down allowed the O₂ molecules to dissociate into oxygen ad-atoms on the surface, the O₂ desorption peak expected at around 100 °C (c.f. Figure 1c) was not observed in the experiment.

The desorption of molecular oxygen as predicted by metastable surface phase diagram in Figure 1c has indeed been observed experimentally. In a TPD study on the catalytic combustion of volatile organic compounds (such as acetone, isopropyl alcohol, and benzene) on LaMnO₃ surface, a desorption peak corresponding to O₂ molecules was observed.⁵¹ The reported peak position was centered slightly above 100 °C, in good agreement with the predictions made in the present study.

Finally, as briefly discussed in section I, according to the Sabatier principle the phase boundaries on the surface phase diagrams are expected to represent the regions of high catalytic activity. At the oxygen ad-atom rich side of the phase boundary on the equilibrium surface phase diagram, plenty of loosely bounded dissociated oxygen ad-atoms are available on the surface, and therefore one might expect that the catalytic activity of the surface toward an oxidative reaction would peak in this regime. In fact, we find that the experimentally observed activity of the LaMnO₃ surface toward NO oxidation indeed shows a peak near the oxygen ad-atom rich side of the predicted phase boundary between clean and 100% O ad-atom covered surface regions (c.f. Figure 1c) on the equilibrium surface phase diagram.¹⁰

V. SUMMARY

A multiscale model combining first principles DFT computations with kMC simulations is presented to study oxygen adsorption, desorption, dissociation, and surface diffusion on the $LaMnO_3(001)$ surface at finite temperatures and pressures. In calculating the equilibrium and metastable (p, T) surface phase diagrams using the kMC simulations based approach, rates of the relevant elementary reactions are described within the transition-state theory. Lateral interactions between the surface-adsorbed species and the effect of the local chemical environment on the reaction kinetics were properly taken into account in the kinetic simulations. The key merit of this multiscale approach is that it allows us to capture kinetic effects such as metastability and sample history by efficiently following dynamics of the system from picoseconds up to seconds. Furthermore, microscopic insight into the system can be gained by simultaneously accounting for the atomic-scale correlations, fluctuations, and spatial distributions of oxygen ad-atoms and ad-molecules at the surface.

A close resemblance between the kMC-simulated and the FPT-based surface phase diagrams shows that the configurational entropic effects due to O ad-atoms on the surface do not play a crucial role in determining the phase diagram. Nevertheless, configurational entropy may play a crucial role in stabilizing partially covered O ad-atom surface configurations to a wider range of pressures and temperatures.

Molecular and associative desorption peaks for surface oxygen observed in TPD experiments are found to be in close agreement with our predictions using the calculated (p, p)T) surface phase diagrams, providing an indirect validation for our computational approach adopted in the present study. Furthermore, following the Sabatier principle the phase boundaries on the (p, T) surface phase diagram are expected to correlate well with the high catalytic activity toward oxidation reactions. We indeed find that the experimentally observed activity of the LaMnO3 surface toward NO oxidation shows a peak near the oxygen ad-atom rich side of the predicted phase boundary. We believe that such a remarkable agreement with available experimental data, despite the approximate nature of the employed semilocal exchangecorrelation functional, can partially be attributed to a favorable error cancellation in the calculation of the surface binding energy in eq 1.

Finally, we note that while the FPT approach may, in general, be sufficient if one is interested in capturing thermodynamic effects alone, the importance and necessity of the kMC approach should be emphasized if one wishes to make connections with experimental observations (which are replete with metastable situations) in a high-fidelity manner.

ASSOCIATED CONTENT

S Supporting Information

First principles thermodynamics approach, details of the elementary processes and evaluation of the rate constants, models for adsorbate—adsorbate lateral interactions, and cross-validation results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon work supported by the Department of Energy. Partial computational support through a National Science Foundation Teragrid allocation is also gratefully acknowledged.

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