NO oxidation properties of Pt(111) revealed by *ab initio* kinetic simulations

S. Ovesson,[1] B. I. Lundqvist,[1] W. F. Schneider,[2,*] and A. Bogicevic[2]
[1]*Department of Applied Physics, Chalmers University of Technology and Göteborg University, S-412 96 Göteborg, Sweden*
[2]*Scientific Research Laboratories, Ford Motor Company, Dearborn, Michigan 48124, USA*
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As a well-known oxidation catalyst, platinum is currently being used to convert NO to NO_2 for absorption in so-called NO_x traps under excess oxygen conditions, where direct conversion of NO to nitrogen gas is prohibitive. By performing kinetic Monte Carlo simulations with parameters derived from density-functional theory, we show that this oxidation process is not an inherent property of the platinum catalyst itself. In fact, the intrinsic $NO+O \rightarrow NO_2$ reaction is found to be inhibited (endothermic) rather than promoted on Pt(111), due to strong oxygen–platinum bonds. Only at sufficient oxygen chemical potential does platinum become an efficient oxidation catalyst, as its oxygen bonds are weakened with increasing coverage, and the NO_2 formation reaction becomes exothermic. At that point, Pt catalyzes the reaction by lowering the activation barrier for the kinetic reaction. Congruent with flow-reactor experiments, we note a strong temperature dependence for the turnover frequency, which should encourage further ultra-high vacuum studies.

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I. INTRODUCTION

Increasingly more stringent emissions and fuel economy requirements have spurred the introduction of lean-burn gasoline and diesel engines, in which hydrocarbons are combusted in excess (above stoichiometric) atmosphere of oxygen.[1] Conventional three-way catalysts, which operate very well in traditional powertrains, are unfortunately ineffective in removing nitrogen oxides (NO_x, $x=1-2$) from the exhaust gas under such conditions. One way around this predicament is to induce selective catalytic reduction of NO_x by means of injection of urea or some other reductant into the catalytic converter.[2,3] Another approach which has gained considerable attention is the temporary chemical trapping of NO_x under lean conditions and subsequent release during brief excursions to reducing (fuel-rich) conditions.[4,5] Both approaches rely fundamentally on the ability to catalytically oxidize NO, the primary component of NO_x from the combustion process, into NO_2. Typically, noble-metal catalysts are used for this purpose, but it is presently unclear as to what limits their activity and how they interact with the oxide supports. Theoretical investigations have traditionally been performed using first-principles or simpler semiempirical molecular modeling. The former approach provides energetics and reaction barriers with chemical accuracy, while the latter lacks such accuracy but instead provides a probe into more relevant size and time scales. Here we present a hybrid approach that combines the advantages of either method, providing significant new insight into the oxidation reaction and the means to separate intrinsic catalytic properties from the effects of varying thermodynamic conditions.

In heterogeneous catalysis, reaction rates for the formation of chemical bonds are seldom just diffusion limited, and the reaction kinetics therefore often depend on residence times in precursor states that are very sensitive to adsorbate interactions. A theory aiming to quantitatively assess complex reaction kinetics must be able to take into account these effects over relevant time and length scales. The magnitude and extent of both direct and indirect adsorbate interactions have been studied previously.[6–8] In the present work, such interactions are quantified from first principles for a three-component system and incorporated into our simulations. Extending the realm of first-principles investigations from the time and length scales of atom dynamics to those of technologically relevant chemical processes like epitaxial growth and catalytic reactions always represents an outstanding challenge. A computationally intensive but quite useful approach is to combine density-functional theory (DFT) and kinetic Monte Carlo (KMC) simulations. This methodology has been exemplified in several recent studies of epitaxial growth of single-component metal and semiconductor systems.[9–12] Because this approach requires an extensive mapping of the elementary processes involved and an accurate calculation of their activation energies, it has yet to make an instep into even more complex areas like catalysis.

In this paper, we present a successful generalization of the DFT-KMC method to a catalytic reaction: the oxidation of NO on Pt(111). The study encompasses a detailed assessment of the energetics, mass transport, and reaction kinetics of O, NO, and NO_2 over Pt(111). The main result is the determining role the oxygen coverage plays in determining the direction of the NO oxidation reaction. To assess the feasibility of using simpler pairwise models for studying systems of this complexity, we also perform a detailed analysis of lateral adsorbate interactions.

II. COMPUTATIONAL DETAILS

As in all KMC simulations, it is important to first determine what elementary processes, here diffusion, reaction, and desorption steps, are likely to be important in the reaction process. By combining existing data on surface intermediates with detailed balance and chemical intuition, we have deduced a list of salient reactions, further discussed below.

TABLE I. Adsorption energies E_a in eV and adsorption heights d_a in Å above the plane averaged over all surface atoms with five (5L) and four (4L) surface layers, respectively.

	E_a^{5L}	E_a^{4L}	d_a^{5L}	d_a^{4L}
N	4.72	4.69	1.00	1.00
O	4.39	4.36	1.16	1.13
NO	1.44	1.28	1.92	1.89
$NO_2^{(i)}$	1.44	1.28	2.36	2.35
$NO_2^{(ii)}$	1.34	1.24	2.59	2.58
$NO_2^{(iii)}$	1.34	1.23	2.58	2.61
$NO_2^{(iv)}$	1.36	1.20	2.40	2.43

The rate of each reaction (including adsorption, diffusion, and desorption) is calculated within transition-state theory using DFT-derived activation energies. The DFT calculations encompass a supercell plane wave pseudopotential method within the PW91 implementation of the generalized gradient approximation (GGA).[13,14] The computational details are described in Ref. 15, unless otherwise noted. The supercells are constructed of four 4×4 (111) Pt layers, the top two of which are fully relaxed and the other two frozen at bulk crystal positions, and five vacuum layers, and the Brillouin zone is sampled with a uniform 3×3 **k**-point mesh.

Transition states for the diffusion and reaction processes are calculated with the nudged elastic band (NEB) method,[16] with four system replicas used between initial- and final-state geometries to achieve a smooth minimum-energy path upon relaxation, determining the activation energies via spline fits. For adsorbate diffusion(O, NO), the transition states are quite simple, located near the geometric saddle points, while for surface-mediated chemical reactions, the minimum-energy paths and transition states are highly complex, as described further below.

III. ADSORPTION ENERGETICS

On the Pt(111) surface, O and NO have previously been shown to adsorb preferentially at fcc threefold hollow sites, the latter N-down and normal to the surface.[15,17]. The calculated adsorption energies at $\Theta=1/16$ monolayer (ML) (where unit coverage is defined as one adsorbate per surface Pt atom), using the four-layer slab model (Table I), correspond well with previous calculations at $\Theta=1/9$ ML,[15] using five-layer slabs. A supercell with four substrate layers is thus deemed sufficiently accurate for the present purposes.

While the determination of the preferred O and NO adsorption structures is relatively straightforward, NO_2 adsorption is more complex and less well understood. Here we investigate a number of O-down, N-down, and NO-down NO_2 adsorption geometries oriented along the $\langle110\rangle$, $\langle111\rangle$, and $\langle112\rangle$ directions: (i) NO-down atop along $\langle110\rangle$, where the second O atom points up and away from the surface, (ii) N-down atop with two O atoms in bridge sites along $\langle110\rangle$ toward the vacuum, (iii) N-down atop with the O atoms in fcc and hcp sites along $\langle112\rangle$, and (iv) the O atoms down in top sites along $\langle110\rangle$ and N above in the bridge site in between. The minimum-energy geometry is (i) (shown in Fig. 1), conventionally labeled μ-N,O-nitrito, in excellent agreement with HREELS data.[18]

TABLE II. Interaction energies in eV and interaction-induced relaxations in Å for O, NO, and NO_2 adsorbates on Pt(111). Interactions beyond 3-NN separation are ignored. Interaction energies $E_{XY}^{\rm int}$ are given in eV as $E_{XY}+E_{\rm slab}-E_X-E_Y$, but reduced by 1/2 for third nearest neighbors to correct for periodic image interactions. $d_{\rm rel}$ is the amount of spatial repulsion induced by adsorbate interactions.

	1-NN		2-NN		3-NN
	$E^{\rm int}$	$d_{\rm rel}$	$E^{\rm int}$	$d_{\rm rel}$	$E^{\rm int}$
N-N	0.36	0.30	0.09	0.02	0.04
O-O	0.20	0.20	0.10	0.02	0.02
NO-NO	0.31	0.24	0.12	−0.00	0.06
NO-O	0.24	0.22	0.10	0.03	0.03
$O\text{-}NO_2^{(i)}$	0.10	0.82	0.10	0.72	0.06
$O\text{-}NO_2^{(ii)}$	0.07	0.09	0.06	0.01	0.03
$O\text{-}NO_2^{(iii)}$	0.06	0.07	0.07	0.01	0.02
$O\text{-}NO_2^{(iv)}$	0.35	0.53	0.09	0.01	0.02

The parameters used in the low-coverage KMC simulations for the rates of all the elementary processes, including diffusion, chemical reactions, and desorption, are computed within DFT (Table II). A common prefactor of 10^{13} Hz is adopted for all processes. A rigorous computation of the diffusion prefactor from first principles and transition-state theory[19] gives values around 10^{13} Hz. The general use of a value like this can be justified by noting that the rates depend exponentially on the activation energies and linearly on the prefactors. At the substrate temperatures considered in this study, prefactor variations of one to two orders of magnitude, which is at most what one expects, will still have a lesser impact on the reaction rates than the variations we expect from the small, but more important errors in our activation barriers.

IV. PAIR INTERACTIONS

In the high O_2 concentrations characteristic of lean exhaust, a significant oxygen coverage of the noble metal is expected. The lateral NO-O interactions under such conditions are therefore of principal interest and call for quantification. Pair interaction energy values are here computed for interactions between O, NO, and NO_2 on Pt(111) (Table II). The adsorbates are kept in threefold fcc hollows unless otherwise noted, and the counting of neighbors is made with respect to the fcc lattice.

In first nearest-neighbor (1-NN) configurations, the interactions are generally repulsive and of the order of 0.2–0.3 eV (except $O\text{-}NO_2$, see below), i.e., quite considerable. Already in next-nearest (2-NN) configurations, adsorbate interactions are much weaker, by a factor of 2–4, and in 3-NN configurations all interaction energies are less than or

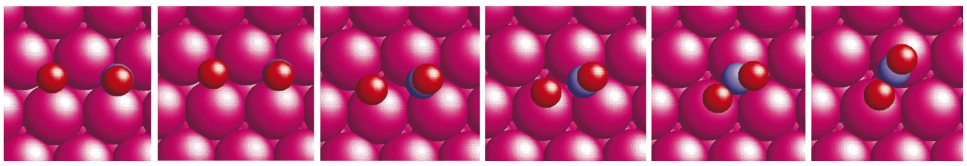

FIG. 1. (Color) Top view of the minimum-energy path for NO_2 formation from NO and O, as computed within DFT-GGA and NEB. The O atoms are colored red and the N atom blue.

about 0.05 eV. The interaction-induced adsorbate relaxations are all found to be 0.2–0.3 Å at the shortest separations, but only a tenth of that for 2-NN.

For the O-NO_2 entries, the designations 1-NN, 2-NN, etc., are made with respect to the fcc site closest to the NO_2, for which reason the interaction energies are not strictly comparable with those of the other molecule pairs. The important observation, however, is that the O-NO_2 interactions are quite weak in all configurations, as expected, given the stability of NO_2.

If interactions beyond the 3-NN separation and many-body contributions can be neglected, the interaction energetics V_i^{XY}, i.e., the pair interaction energy for species X and Y at ith nearest-neighbor separation (Table II), determines the ground-state adsorbate patterning of the surface. For the O/Pt(111) system, the inequalities $V_3>0$, $V_1>3V_3$, and $V_2>2V_3$ hold, and the $p(2\times2)$ structure is then predicted at $\Theta=25\%$.[20]

This is in good agreement with experimental findings.[21]

V. NO VS NO_2 STABILITY

In the gas phase, the reaction $NO+1/2O_2\rightarrow NO_2$ is exothermic by 1.20 eV. On the clean Pt(111) surface, the O_2 dissociates at 150 K,[22] and the oxidation reaction $NO+O\rightarrow NO_2$ is instead *endothermic* by 0.7 eV. Thus *Pt(111) by itself does not catalyze NO oxidation!* However, with increasing O coverage the energetics is changed in favor of NO_2, due to strong repulsive O-O and O-NO interactions. The sample calculations presented in Fig. 2 and Table III illustrate this: For an NO in a saturated O $p(2\times2)$ overlayer (i.e., removing an O from the $p(2\times2)$ structure to form NO_2, from configuration 12 to 13 in Fig. 2), the reaction is nearly isothermic. Increasing the initial O coverage (i.e., before adding NO) to 5/16 (from configuration 14 to 15) the NO_2 becomes favored by 0.28 eV.

It is thus clear that the $NO\rightarrow NO_2$ conversion on Pt(111) is driven by lateral adsorbate interactions. To accurately predict the kinetic consequences of these interactions, one needs to explore a larger fraction of the full configuration space beyond the sample calculations displayed in Fig. 2. Reaction energetics and kinetics can both be assessed in KMC simulations if, in addition to clean-surface activation energies, the interaction energetics can be properly accounted for. Pairwise summation of interaction energies would be a tractable solution apt for KMC implementation.

Using the computed interaction energies (Table II), pairwise summation is performed for more complex adsorbate configurations. The expansion of the energy in terms of pair interactions is truncated at the 3-NN separation. The various configurations considered are displayed in Fig. 2, and the energies appear in Table III. Pairwise summation with 3-NN interactions works rather well, with errors smaller than 0.10 eV per atom even at the highest coverages and/or most frustrated geometries (i.e., those allowing the least lateral relaxation).

VI. KINETICS OF NO OXIDATION

In order to assess the kinetic effects of lateral interactions and O coverage on the $NO+O\rightarrow NO_2$ conversion in oxygen-rich environments, we perform a set of first-principles KMC simulations[23] of NO deposition on the O-precovered Pt(111) surface. The activation energies are calculated with DFT, as reported here and in Ref. 15

The relevant (i.e., not too rare) processes are O diffusion (activation energy=0.56 eV), NO diffusion [0.24 eV; diffusion barrier for N is found a little high (0.81 eV)], NO_2

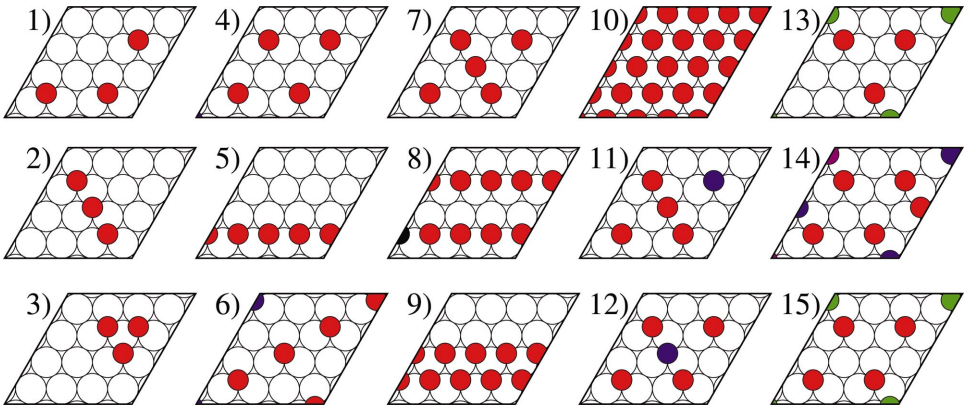

FIG. 2. (Color) Adsorption geometries considered besides those used for the computation of Tables I and II. All adsorption occurs in threefold fcc hollows. The colors red, blue, and green denote O, NO, and NO_2 adsorbates, respectively.

TABLE III. Energies in eV for the adsorbate configurations displayed in Fig. 2. To facilitate comparisons, the zero of the energy scale is set to $E_0 = m \cdot E_N^1 + n \cdot E_O^1 - (m+n-1)E_{slab}$, where E_N^1 (E_O^1) is the energy of an isolated N (O) atom adsorbed on a clean slab, and m (n) denotes the number of N (O) *ions* in the cell, so that $E_0 = 0$, if no interactions are present. The energy given is $E_{int} = (E - E_0)/(m+n)$. E_{PW} is the value of E_{int} predicted, if interactions are pairwise additive and negligible beyond third-nearest-neighbor separation.

No.	E_{int}	$E_{int} - E_{PW}$	No.	E_{int}	$E_{int} - E_{PW}$
1	0.03	−0.00	9	0.49	−0.03
2	0.15	0.01	10	0.99	0.02
3	0.21	0.00	11	0.10	−0.05
4	0.04	−0.01	12	0.12	−0.01
5	0.25	0.03	13	0.13	0.09
6	0.10	−0.03	14	0.18	−0.05
7	0.14	0.02	15	0.14	0.07
8	0.32	0.07			

formation (1.25 eV), NO_2 decomposition (0.90 eV), and NO_2 desorption (1.28 eV).

The most complex reaction in this study is $NO + O \rightarrow NO_2$. It starts with an upright N-down NO molecule adsorbed in an fcc site with an oxygen atom in a neighboring fcc site and ends in the μ-N,O-nitrito NO_2 configuration, i.e., with all fragments in their energetically preferred sites. Because of its higher mobility,[15] the reaction proceeds with the NO molecule diffusing towards the adsorbed O atom via a bridge site, as depicted in Fig. 1. As the NO crosses the bridge site and the two fragments are about 2.5 Å away, the adsorbed O atom has already moved about 0.8 Å to accommodate the formation of a chemical bond. We find the activation energy for this process to be about 1.25 eV at low coverage, noting that this value is likely sensitive to the local adsorption environment and that there may be lower-energy reaction pathways.

Coverage effects are accounted for by summing pair interactions in initial and final configurations up to 3-NN separations and then adjusting barrier energies with a simple interpolation formula,[24]

$$E_A = E_A^0 + \tfrac{1}{2}(E_f - E_i), \tag{1}$$

where E_A^0 is the low-coverage limit of the activation energy, and E_f and E_i are the total interaction energies of the final and initial states of the motion, respectively. All prefactors are set to 10^{13} Hz.[25] At high temperatures, adsorbate diffusivities are suppressed by a common factor to reduce CPU time consumption; convergence with respect to this parameter is carefully checked.[26]

For oxygen, the fcc hollow site is preferred by 0.41 eV over the hcp site. We find this preference to increase when the surface is precovered with a $p(2\times2)$ O overlayer, in contrast to a recent thermal desorption study.[27] For NO, the fcc-hcp difference is smaller (0.10 eV), but the NO diffusion is found to be of minor importance for the reaction kinetics. As for NO_2, the fact that it does not bind in registry with the substrate has little influence on the kinetics, as there is always one fcc site in the proximity of the NO_2, where no adsorption is possible, and that site can then be treated as occupied by the NO_2.

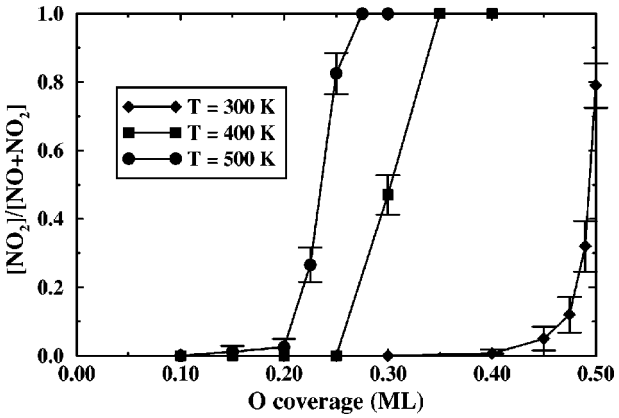

FIG. 3. Efficiency of the NO oxidation process as a function of initial oxygen coverage and temperature on Pt(111). Statistical errors of two standard deviations are indicated.

Hence, in the KMC simulations fcc sites only are considered.

Adsorbates move on a triangular lattice with periodic boundary conditions containing 40×40 sites. Oxygen atoms are first deposited at random on the clean surface, and the system is equilibrated for 1 s. With the focus on the dilute limit of NO abundance, exactly one NO molecule is then deposited, and the system is annealed for another 2 s. Within this time NO_2 may form, decompose, and desorb.

VII. KINETICS

The computed final fraction of NO_2 (at the surface and in the gas phase) as a function of temperature and initial oxygen coverage (Fig. 3) shows unexpected features: The NO oxidation reaction turns on at about 0.2 ML O coverage for the highest temperature considered but requires up to 0.25 ML more oxygen at 300 K. This is mainly a kinetic effect, as at 300 K the opposite reaction does not take place for any coverage above 30%. At 0.20 ML O coverage the oxidation reaction does not occur to an appreciable extent for any temperature—as expected from the sample DFT results discussed above—but the enhancement of the reactivity with increasing Θ_O is strongly temperature dependent.

Thus, at high temperatures, the reaction can be driven back and forth with slight changes in the O coverage around 0.25 ML, whereas at low temperatures, large changes are required for kinetic reasons. The NO_2 formation reaction is thus activated by both temperature and the accumulation of O atoms around the NO.

Given the strong sensitivity of the oxidation efficiency to the oxygen coverage, there is good reason to investigate experimentally or theoretically the external conditions for bringing the system slightly above or below the critical coverages.

VIII. CONCLUDING REMARKS

In conclusion, the $NO \leftrightharpoons NO_2$ reaction on an O-covered Pt(111) substrate is studied using first-principles KMC simulations. The catalytic activity is found to depend strongly on the oxygen coverage. The surface reaction is highly endothermic in the low-coverage limit but turns exothermic at $\Theta_O \approx 25\%$, due to repulsive lateral O-O and O-NO interactions. However, for kinetic reasons, as much as 0.45 ML O coverage is required for the reaction to be activated at room temperature. These findings are congruent with flow-reactor experiments[28] and should encourage future ultra-high-vacuum studies.

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*Present address: Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA.

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