

The Role of Surface Oxides in NO_x Storage Reduction CatalystsJelena Jelic,^[a, b] Karsten Reuter,^{*[b]} and Randall Meyer^{†[a]}

The need for greater fuel economy in automotive vehicles has driven a surge in the development of diesel and lean-burn gasoline engines. Coupled with the increase in fuel efficiency, an increase in the air to fuel ratio also results in heightened production of NO_x.^[1] Several different strategies have been proposed for the handling of the higher NO_x levels in lean-burn automotive emissions. One such strategy is the NO_x storage reduction (NSR) system whereby excess NO is further oxidized to NO₂ over the exhaust catalyst, which is typically platinum, and then NO₂ is stored on a carrier material, such as BaO.^[2] The catalyst system operates in this fashion for some minutes until the storage material has been fully converted. The system then cycles to a rich mode, during which a reductant is injected into the exhaust stream and reacts with the stored NO_x, possibly at the interface between the carrier material and the metal particle, to produce the traditional exhaust products of N₂, H₂O, and CO₂, all in a matter of seconds. Therefore, a requirement of a successful NSR catalyst is that the catalyst must be active for both NO oxidation and NO_x reduction.

In recent years, a debate has emerged as to the role of metal oxides in oxidation catalysis.^[3–6] Although there have been some indications that oxide surfaces may be more active in simple oxidation reactions such as CO oxidation,^[7] platinum catalysts have been preferred as the metal component in the NO_x storage reduction system for their combination of high activity and ability to resist deactivation through oxidation. Ribeiro et al. have studied Pt NO-oxidation catalysts for NSR applications in considerable detail. They determined that large Pt particles are more active and that single crystal Pt(111) and Pt(100) outperform disperse Pt particles.^[8,9] One possible explanation for the higher activity of the single crystal surfaces is that oxygen is bound less strongly and that the catalysts do not deactivate due to oxide formation. Reports of platinum deactivation as a NO oxidation catalyst, however, concern catalysts that have been exposed to oxygen (and NO) for long periods.^[9] As NSR systems operate under a cyclic operation scheme, whereby thermodynamics may not be a controlling factor, it is not clear if the formation of bulk oxides is truly a concern.

Recent experiments by Amiridis, Harold, and co-workers performed under actual operating conditions indicated that Pd outperforms Pt in the critical low temperature regime that cor-

responds to engine startup.^[10] Since the reduction reactions are considered to be very fast as compared to the oxidation of NO, and the performance of the reduction regime is likely mass transfer limited,^[11] the superior performance of Pd must be related to its ability to perform NO oxidation. Given this result, one may ask if Pd, which surely oxidizes more easily than Pt,^[12,13] could be a viable NSR catalyst and, if Pd were used, what the surface of the working catalyst is likely to be under operating conditions.

We have previously examined the phase diagram for Pd(100) and Pd(111) and found that, under the typical NO oxidation mode of a NSR catalyst (600 K, 10⁵ Pa O₂, 100 Pa NO), the bulk oxide is the thermodynamically preferred state.^[14] However, grazing incidence X-ray diffraction results from Lundgren et al. indicated that, under steady-state conditions of 600 K and 1 atm O₂ (1 atm = 101 325 Pa), kinetic limitations prevent transformation of a monolayer surface oxide film to the bulk oxide on time scales in excess of one hour.^[15] In the case of NO oxidation, this transformation of the surface oxide to the bulk oxide should be even more difficult, as NO is present as a reductant (albeit a weak reductant).

We have performed kinetic Monte Carlo (kMC) simulations of NO oxidation on the PdO(101)/Pd(100) surface oxide system^[16] to determine a typical turnover frequency for Pd catalysts in an effort to understand the results of Amiridis, Harold, and co-workers, which indicated the superior performance of Pd.^[10] From the work of Lundgren et al., it seems likely that a surface oxide is the best model to describe the Pd surface.^[15] It should be recognized that the choice of the underlying Pd surface is not likely to be critical as a PdO(101) film grows on both Pd(100) and Pt(111) under oxidizing conditions.^[16] Furthermore, upon oxygen adsorption, the Wulff construction of a Pd particle changes to increase the number of Pd(100) facets as the overall energy is lowered by the favorable interaction between oxygen and the Pd(100) surface.^[17]

In first-principles kMC simulations, we follow the time evolution of the system as described by a master equation and use rate constants for the individual elementary processes that are obtained from density functional theory (DFT) calculations.^[18,19] We specifically use a lattice kMC model for the PdO(101)/Pd(100) surface oxide that was developed in CO oxidation studies by Rogal and co-workers.^[20,21] This lattice structure, which includes bridge and hollow adsorption sites, is depicted in Figure 1. The surface oxide unit cell contains two hollow and two bridge sites. Although the two bridge (or hollow) sites are not identical, our calculations indicated that adsorption of oxygen (or NO) are similar, allowing us to simplify the unit cell of the surface oxide and create a new, smaller unit cell for the kMC simulations by halving the surface unit cell (white dotted line in Figure 1).

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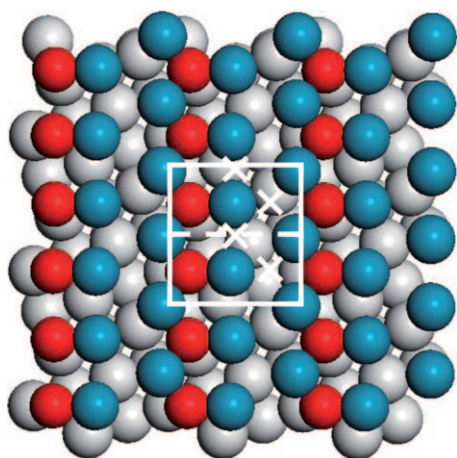


Figure 1. The PdO(101)/Pd(100) kMC lattice. Red atoms are oxygen, dark blue atoms are Pd in the surface oxide layer, and gray atoms are Pd atoms in the bulk [Pd(100)]. The white square represents the surface oxide unit cell. The dotted line indicates the split of the oxide unit cell into two smaller cells as discussed in the text. White crosses represent the considered adsorption sites—hollow and bridge sites.

The kMC simulations were performed for fixed (T , p_{O_2} , p_{NO}) conditions on a periodic lattice consisting of 100 bridge and 100 hollow sites, evaluating the average occupation at the various surface sites after steady state was reached. Following this path, we first checked the stability of the surface oxide in the range of $p_{NO} = 10^{-5}$ – 10^5 atm for $p_{O_2} = 1$ atm and $T = 600$ K, where decomposition of the surface oxide is expected. As an indicator of the oxide structural stability, we determine the average occupation of the hollow sites by oxygen, $\bar{\theta}_{O^{hol}}$, which is 100% in the intact oxide^[20,21] If the occupation decreases below 95% we consider this as a sign of the onset of the structural decomposition.

The barrier for dissociative O_2 adsorption is 0.41 eV for hollow–hollow sites and 0.52 eV for bridge–hollow sites, but is 1.9 eV across two bridge sites. There are four possible ways to perform NO oxidation, but only two are important for our system: $NO^{hol} + O^{br}$, with a computed barrier of 0.54 eV, and $NO^{br} + O^{hol}$, with a barrier of 1.08 eV. Although the former reaction step has a significantly lower barrier, the latter process is found to dominate the kinetics of our system due to the strong preference for oxygen to occupy hollow sites, which forces any NO to adsorb on bridge sites. NO oxidation slightly lowers the critical pressure for surface oxide decomposition compared to our preceding thermodynamic study (Figure 2),^[14] but for a typical NO pressure of 100 Pa the surface oxide is stable. Even if we artificially lower this barrier to 0.98 eV to account for possible DFT inaccuracies, the surface oxide remains stable in essentially the same pressure range. Furthermore, in contrast to CO_2 , the NO_2 desorption energy is not negligible ($\Delta E = -1.15$ eV). Therefore NO_2 desorption, as well as dissociative readsorption of NO_2 , must be included since NO_2 formation is endothermic ($\Delta E = 0.5$ eV). In spite of this, NO_2 readsorption does not greatly affect the turnover frequency (TOF) as NO_2 desorption is a single-site process, whereas two sites are

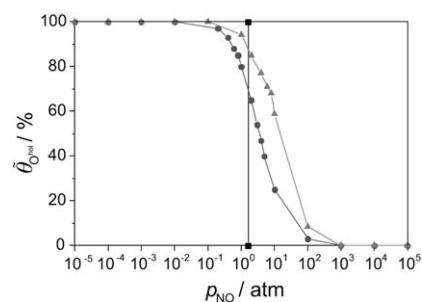


Figure 2. Kinetic Monte Carlo results for the stability of the surface oxide: average occupation $\bar{\theta}_{O^{hol}}$ of the hollow sites with oxygen on the kMC lattice vs. the NO partial pressure. Average occupation decreases to below 100% only for NO pressures much higher than those relevant for NSR (see text). This finding is unaffected, if the most relevant activation barrier for the $NO^{br} + O^{hol}$ reaction is reduced from the calculated value of 1.08 eV to 0.98 eV. The vertical line represents the stability limit of the surface oxide as deduced from ab initio thermodynamic considerations (Ref. [14]).
● $E_a = 0.98$ eV; ▲ $E_a = 1.08$ eV; $T = 600$ K; $p_{O_2} = 1$ atm (1 atm = 101 325 Pa).

needed for NO_2 dissociation, implying that, at high O coverage, desorption is preferred.

With the stability of the surface oxide confirmed, we determined that the steady-state TOF of our PdO(101) surface at $T = 600$ K, $p_{O_2} = 10^5$ Pa, $p_{NO} = 10^{-3}$ bar, and $p_{NO_2} = 10^{-3}$ bar is $0.80 \text{ site}^{-1} \text{ s}^{-1}$. This value compares favorably with previous results from Ribeiro and Schneider in their examination of Pt(111) surfaces (TOF = $0.34 \text{ site}^{-1} \text{ s}^{-1}$ determined both experimentally and from a first-principles microkinetic model) indicating that the Pd surface oxide activity is comparable to that of platinum metal.^[8] In this respect, it is intriguing to note that Schneider et al. used a mean-field microkinetic model to describe the NO oxidation on Pt(111) and achieved remarkable agreement with the experimental results. However, the resting state of the Pt(111) surface in this model has a very high oxygen coverage (0.625 ML), which is higher than the maximum coverage of oxygen in an oxygen atmosphere alone and could potentially transform to the surface oxide.^[22]

Although our work indicates the surface oxide of palladium is quite active, previous experimental work has indicated platinum oxide is not active.^[9] Wang et al. have recently examined the NO oxidation using DFT and found that while Pt(111) is more active than $PtO_2(110)$, this situation is reversed for Ir(111) and $IrO_2(110)$ suggesting that the relative activities of the metals and oxides must be examined separately due to the different mechanisms for O_2 dissociation and NO oxidation.^[23] Furthermore, the structures of oxides vary across the fcc metals, so without more detailed examination we cannot say how our model for PdO(101)/Pd(100) will fit into the volcano plot created by Wang et al. to describe the reactivity of $MO_2(110)$ metal oxide surfaces.

Figure 3 shows the temperature dependence of the TOF. The TOF increases with temperature until about 600 K. At this point, the coverage of NO on the surface is too low (or too short-lived) to keep pace with the reaction, further suggesting another reason why NO oxidation must be in a narrow temperature window relative to the potential range of exhaust gas

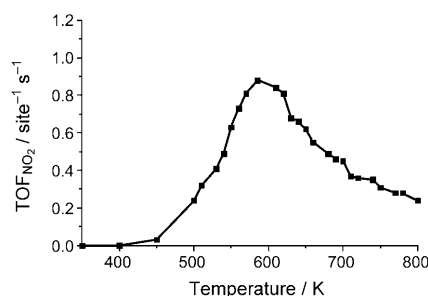


Figure 3. Variations with temperature of calculated steady-state TOF for NO oxidation on the PdO(101)/Pd(100) surface oxide. $p_{\text{O}_2} = 10^5$ Pa; $p_{\text{NO}} = 100$ Pa; $p_{\text{NO}_2} = 100$ Pa.

temperatures. High gas-phase temperatures also lead to NO₂ decomposition as O₂ and NO become the favored thermodynamic products; we do not include the gas phase reaction in our simulations.

Herein, we have demonstrated that a surface oxide may be a viable catalyst for NO oxidation, counter to the conventional wisdom that oxides are inactive as NSR catalysts. Although the latter might qualify for bulk oxides, their formation is avoided by the cycling conditions of NSR. Instead, under the oxidation regime our simulations suggest that the system remains in a thermodynamically metastable state, namely an ultrathin surface oxide film.

Experimental Section

The density functional theory calculations in this work are performed using the Vienna Ab Initio Simulation Package (VASP)^[24,25] and the GGA-PW-91 exchange-correlation functional.^[26] Ultrasoft Vanderbilt pseudopotentials,^[27] a plane wave cutoff energy of 400 eV, and a $7 \times 7 \times 1$ Monkhorst Pack^[28] k-point grid were used in all calculations reported herein. The computational settings are thus identical to those of ref. [14], in which the convergence of the target quantities, in this case the binding energies and reaction barriers, has already been detailed. In the kMC simulations, we consider 34 processes of nonconcerted element- and site-specific adsorption, desorption, diffusion, and surface reaction. Nearest neighbor lateral interactions are taken into account in the elementary process rates and we verified that the kMC formulation reproduces the portions of the thermodynamic phase diagram in the area of interest when the reaction events are not allowed to occur.^[29]

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