Coverage Effects for the CO Oxidation Reaction on O-Rich Pd(111)

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Introduction

The CO oxidation reaction is crucial in the function of catalytic converters found in personal vehicles. Despite its simplicity, several aspects of this reaction are still under investigation. Thus, a recent experimental study by Nakai *et al.* [1] proposed that CO oxidation on O-precovered Pd(111) exhibits markedly different rates at different temperatures as a result of different phases in the O overlayer exhibiting disparate reactivities. Thus, the $p(2\times2)$ phase appears as inert, whereas the $(\sqrt{3}\times\sqrt{3})R30°$ and $p(2\times1)$ are reactive and exhibit distinct apparent activation energies and reaction orders with respect to O coverage. It still unclear however, whether there is a causal relation between the changes in the overlayer structure and the different reactivity, and if this is the case, what is the mechanism giving rise to this effect.

Materials and Methods

We perform first principles-based kinetic Monte Carlo (KMC) simulations using *Zacros*, our software package implementing the Graph-Theoretical KMC approach.[2, 3] The input to the software consists of the simulation conditions, a lattice structure, an initial spatial configuration of adsorbates (corresponding to a $p(2\times2)$ O adlayer), as well as specifications of the adsorbate lateral interactions and the reaction mechanism. For the lateral interactions, a detailed cluster expansion Hamiltonian is used, incorporating pairwise additive terms up to the 3rd nearest-neighbour, as well as 3-body terms, for CO and O species bound to fcc and hcp sites on the Pd(111) surface. The activation energies in the reaction mechanism are expressed via Brønsted-Evans-Polanyi (BEP) relations, in order to explicitly account for the impact of lateral interactions on the rate constants of the elementary events (adsorption/desorption, diffusion and reaction).

Density functional theory (DFT) calculations using the Quantum ESPRESSO software package are employed to parameterise the model. We use the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange and correlation functional, and a plane wave basis set with ultrasoft-pseudopotentials. We adopt a slab geometry, with 4 metal layers, where the bottom two layers are held fixed in bulk positions. A vacuum of 12 Å ensures negligible coupling between periodic replicas of the slab. Nudged elastic band (NEB) calculations are used to identify the transition states of the CO oxidation elementary events for various configurations of spectator molecules, thereby parameterising the BEP relations.

Results and Discussion

Our simulation scheme follows the titration protocol by Nakai *et al.*:[1] the O-pre-covered Pd(111), represented by a 48×48 lattice, is exposed to CO at different temperatures and the coverage profiles and reaction rates are monitored. Our results[4] reproduce quantitatively the main features of the experimental measurements. Thus, at 320 K the coverage of O drops linearly after a short induction period indicating zeroth order kinetics with respect to θ_O, whereas at 190 K no induction period exists and the kinetics exhibit order ½ with respect to θ_O. The apparent activation energies are also predicted successfully by the model in the low and high temperature regions (Figure 1).

The ordering of the adsorbate layer is found to strongly depend on the strength of lateral interactions but does not seem to have a significant role on the catalytic properties of the system. More specifically, the value of the 2nd nearest neighbour O-O interaction is found to affect the emergence of the $(\sqrt{3}\times\sqrt{3})R30°$ phase, with higher values thereof resulting in the absence of this phase throughout the simulated timecourse. Yet, the coverage profiles remain unaffected, indicating that there is no causal relationship between the emergence of different adlayer phases and the variable reactivity.

On the other hand, by analysing the appearance and realisation statistics of the elementary CO oxidation processes, we discover that coverage effects are responsible for shaping the reactivity of the system. Thus, only a small subpopulation of events with rather low activation energies contributes to the observed rate (Figure 2). The active species in these events appears to be loosely bound CO, as a result of the repulsive interactions that destabilise the initial state of the CO oxidation reaction (surface bound CO+O).

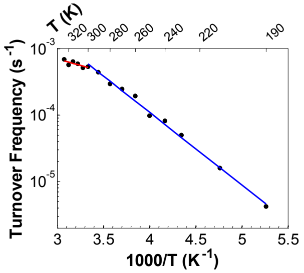

Figure 1. Arrhenius plot for CO oxidation on Pd(111). Apparent activation energy in the high-temperature regime (>300 K, red line): 0.06 ± 0.04 eV (experimental 0.04 ± 0.02 eV). For low-temperatures (≤300 K, blue line): 0.22 ± 0.01 eV (experimental 0.29 ± 0.03 eV). Excellent agreement with experimental data is observed.

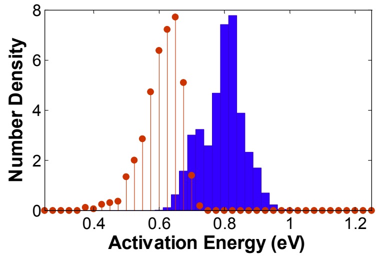

Figure 2. Blue histogram: statistics of activation energies for CO oxidation between fcc-bound CO+O, as calculated from a lattice snapshot taken for T = 190 K at t = 1.4×10^4 s, for which $\Theta(O_{fcc}) = 0.16$, $\Theta(CO_{fcc}) = 0.22$, $\Theta(O_{hcp}) = 0.012$, and $\Theta(CO_{hcp}) = 0.25$ ML. Red stems: activation energy statistics for the CO oxidation events that actually took place up until that time-point.

Significance

Our study demonstrates the power of *ab initio* KMC in providing a quantitative understanding of catalytic kinetics. While the precise knowledge of the adlayer phase does not seem to be critical, our simulations underscore the importance of coverage effects on reaction rate estimation. The local environment of elementary reactions markedly affects their activation energies, to the extent that only a small subpopulation of low-barrier events contributes to the overall rate. This phenomenon has also been previously observed in a model of NO oxidation.[5]

References

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