

## Coupled Theoretical and Experimental Analysis of Surface Coverage Effects in Pt-catalyzed NO Oxidation

W. F. Schneider,<sup>1,\*</sup> R. B. Getman,<sup>1</sup> B. S. Mun,<sup>2</sup> R. M. Rioux,<sup>3</sup> W.S. Epling,<sup>4</sup>  
D. Zemlyanov,<sup>5</sup> A. D. Smeltz,<sup>5</sup> W.N. Delgass,<sup>5</sup> F.H. Ribeiro<sup>5,\*</sup>

<sup>1</sup>University of Notre Dame, Notre Dame, Indiana, 46556 (USA), <sup>2</sup>Lawrence Berkeley National Laboratory, Berkeley, CA 94720, <sup>3</sup>Harvard University, Cambridge, MA 02138, <sup>4</sup>University of Waterloo, Waterloo, Ontario N2L3G1 (Canada), <sup>5</sup>Purdue University, West Lafayette, Indiana, (USA)\*[w Schneider@nd.edu](mailto:w Schneider@nd.edu) and [fabio@purdue.edu](mailto:fabio@purdue.edu)

### Introduction

Catalytic oxidation of NO to NO<sub>2</sub> is a key element of NO<sub>x</sub> emissions control, including the lean NO<sub>x</sub> trap, NO<sub>x</sub> selective catalytic reduction, and the catalyzed particulate filter.<sup>1</sup> Supported Pt is the most common NO oxidation catalyst. Despite the apparent simplicity and superficial similarity to the very familiar CO oxidation reaction, fundamental questions remain about the mechanism of NO oxidation. In this work we use a combination of in situ XPS experiments and first-principles simulations to explore factors that control NO oxidation, in particular the role of oxygen coverage under reactive conditions. We find strong evidence that the surface coverage is controlled by oxidation of the surface by NO<sub>2</sub>.

### Methods

In situ XPS experiments were carried out at the Advanced Light Source at LBNL on a Pt(111) single crystal to determine the uptake of oxygen in the presence of O<sub>2</sub> and NO<sub>2</sub> oxidants. Plane wave, supercell DFT simulations of the Pt(111) surface and its reactions with NO<sub>x</sub> and O<sub>2</sub> were performed with the Vasp code.<sup>2,3</sup> The choice of the Pt(111) surface is motivated by the experimental evidence that turnover frequency increases with increasing particle size,<sup>4,5</sup> implicating the low-energy (111) surface as the active face for NO oxidation.

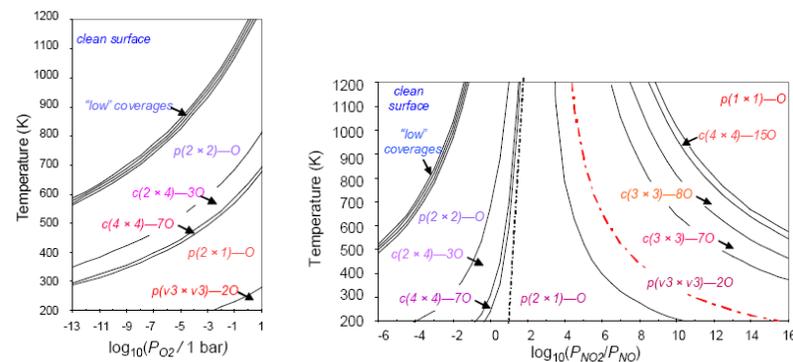
### Results and Discussion

DFT calculations are performed to investigate the stable Pt(111)-NO<sub>x</sub> surface species at low coverage. The results demonstrate, consistent with experimental inference, that catalytic oxidation of NO to NO<sub>2</sub> via O<sub>2</sub> dissociation and reaction is highly endothermic on the clean surface because of the much greater bond strength of Pt-O than O-NO. Catalytic NO oxidation thus must proceed on surfaces with substantially weakened Pt-O bonding, as occurs at higher surface O coverage.<sup>6</sup>

In situ XPS experiments were performed to determine surface coverages under conditions relevant to NO oxidation. In initial calibration experiments, a Pt(111) crystal surface is dosed with O<sub>2</sub> to ¼ ML coverage. NO oxidation produces NO<sub>2</sub>, which is itself a strong oxidant and can potentially participate in further surface oxidation. Experiments in which the Pt(111) surface are dosed with NO<sub>2</sub> confirm this effect, and a surface coverage of 0.77 ML is found. These results are consistent with earlier reaction and surface titration measurements that indicate highest activity near ¾ ML coverage.<sup>4,5</sup>

In order to determine the structure and properties of this high coverage oxygen surface, DFT calculations were performed for a large number of surface O coverages and orderings within different Pt(111) supercells. First principles thermodynamics are used to calculate surfaces phase diagrams as a function of O<sub>2</sub> or NO<sub>2</sub> chemical potential. Figure 1

(left) shows the calculated equilibrium O coverages in O<sub>2</sub>; the ¼-ML p(2×2)-O ordering is prominent at UHV conditions and ½-ML p(2×1)-O at conditions representative of NO oxidation catalysis. Figure 1 (right) shows the calculated O coverage with NO<sub>2</sub> as an oxidant.



**Figure 1.** DFT calculated Pt(111)-O surface coverages in O<sub>2</sub> and NO<sub>2</sub> oxidants.

The stronger oxidizing potential of NO<sub>2</sub> is evident in the higher equilibrium coverages; further, we expect oxidation of the surface with NO<sub>2</sub> to be less kinetically hindered than oxidation by O<sub>2</sub>. The 0.77 ML coverage found experimentally is readily associated with the c(3×3)-7O ordering found with DFT. This coverage is thermodynamically and kinetically inaccessible with O<sub>2</sub> as an oxidant.

Further, calculations indicate that this high-O-coverage surface is metastable to formation of a completely oxidized surface. The high activity of Pt(111) results in part from its kinetic, rather than thermodynamic, resistance to oxidation.

### Significance

Mechanistically, these results imply that surface dissociation of O<sub>2</sub> is not possible at the high surface coverages present during NO oxidation, consistent with O<sub>2</sub> adsorption as the rate-limiting step in catalysis. This evidence indicates that net NO oxidation most likely occurs by direct reaction of NO with adsorbed O<sub>2</sub>, contrary to previous theoretical models for this reaction.

### References

- (1) Gandhi, H. S.; Graham, G. W.; McCabe, R. W. *J. Catal.* **2003**, *216*, 433.
- (2) Kresse, G.; Joubert, J. *Phys. Rev. B* **1999**, *59*, 1758.
- (3) Kresse, G.; Furthmüller, J. *Comp. Mat. Sci.* **1996**, *6*, 15.
- (4) Mulla, S. S.; Chen, N.; Cumaranatunge, L.; Blau, G. E.; Zemlyanov, D.; Delgass, W. N.; Epling, W. S.; Ribeiro, F. H. *J. Catal.* **2006**, *241*, 389.
- (5) Mulla, S. S.; Chen, N.; Delgass, W. N.; Epling, W. S.; Ribeiro, F. H. *Catal. Lett.* **2005**, *100*, 267.
- (6) Getman, R. B.; Schneider, W. F. *J. Phys. Chem. B* **2006**, *110*, in press.