DFT-Based Kinetic Models of Pressure-Dependent Carbonate Poisoning during CO Oxidation over RuO_2(110)

HangYao Wang[1] and William Schneider[2]*
[1]*Department of Chemical and Biomolecular Engineering*
[2]*Department of Chemistry and Biochemistry,*
University of Notre Dame, Notre Dame, IN 46556, USA,
*Email: wschneider@nd.edu

Introduction

Catalytic oxidations with O_2 are one of the most important and widely studied reaction classes in heterogeneous catalysis. Metal oxides are of particular interest as catalysts because of the potential to replace expensive precious metals such as Pt and Pd. Despite the promising catalytic oxidation activities metal oxides have shown, practical applications are limited by surface poisoning such as sulfur or carbonate poisoning, which has been a major concern for metal oxide catalysts for decades [1]. With growing interest in the role of metal oxide films in the oxidation activity of even the more noble metals, it is important to understand and ultimately to learn to bypass surface poisoning.

CO oxidation over RuO_2(110) has been studied extensively as a model for metal oxide catalysis [2]. RuO_2 exhibits high catalytic activity for CO oxidation under UHV conditions [3]. At ambient pressures, however, surface carbonate has been experimentally observed to poison the catalyst [4]. The exact nature of carbonate on this surface and the mechanism of its formation are still unclear. Most importantly, it is not well known under what conditions the carbonate poison forms and under what conditions it can be avoided.

Computational Methods

We develop a kinetic model to investigate the effect of carbonate poisoning on CO oxidation over the RuO_2(110) surface using data obtained from plane-wave, supercell DFT calculations [5]. Calculations were performed using the projector augmented wave (PAW) method within *VASP*. Electronic energies and forces were calculated within the non-spin-polarized generalized gradient approximation (GGA) using the PW91 functional.

Results and Discussion

Initial DFT calculations identify two types of stable surface carbonates on RuO_2(110), arising from CO_2 binding at bridge and cus oxygen sites. The latter are the more stable and exhibit a vibrational spectrum consistent with experimental observation [6]. We write a CO oxidation mechanism incorporating the formation of surface carbonates:

$O_2(gas)+2^* \leftrightarrow 2O^*$ (1)
$CO(gas)+^* \leftrightarrow CO^*$ (2)
$CO^*+O^* \leftrightarrow CO_2(gas)+2^*$ (3)
$CO_2(gas)+O^*+^* \leftrightarrow CO_{3,cus\text{-}cus}^{**}$ (4)
$CO_2(gas)+O_{br}{}^*+^* \leftrightarrow CO_{3,cus\text{-}br}^{**}$ (5)

Carbonate formation steps (4) and (5) are found to have modest activation energies. Reaction (3) has the largest activation energy (0.89 eV) in the network and is the rate determining step (RDS) under conditions of interest. Assuming quasi-equilibrium for all other steps, the network is solved as a function of temperature and overall approach to equilibrium γ for a range of CO and O_2 pressures.

The computed log of CO oxidation turnover frequency at moderate temperature and approach to equilibrium is shown in Figure 1(a). The log(TOF) exhibits volcano-like behavior in both CO and O_2 pressures. Compared to a model neglecting carbonate poisoning, the rates at high O_2 and CO pressures (upper-right corner) are reduced by several orders of magnitude.

To illustrate how the surface is poisoned by various species at various reaction conditions, we label the region where a surface species has coverage more than 0.95 in Figure 1(b). The high carbonate coverage in the upper-right corner leads to an extremely small CO_2 formation rates as shown in corresponding region in Figure 1(a). We find that the ambient pressure condition used in experiments [4] in which carbonate formation has been observed fall into the "Carbonate" region as labeled by the diamond symbol in Figure 1(b). On the other hand, the UHV experiments [3] in which CO oxidation have been observed fall into the white region corresponding to the peak area for CO_2 formation rate in Figure 1(a). The consistence with the experiments lends support for the validity of the kinetic model.

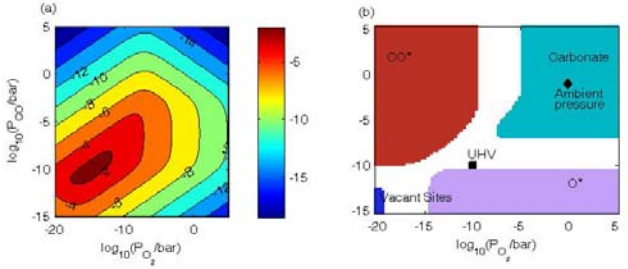

Figure 1. (a) Contour map of turn-over frequencies log(TOF/(site^{-1}s^{-1})) for CO_2 formation including carbonate poisoning at T=350 K and $\gamma=(1/K_{eq})^{1/2}$. (b): Regions of individual species coverage greater than 0.95.

Significance

The DFT-based kinetic model developed here explains the apparent poisoning "pressure gap" observed in CO oxidation over RuO_2(110). Similar mechanisms are expected to be important in oxidations over other metal oxides, including those generated *in situ*, and in oxidations of other adsorbates, such as NO or SO_2. Design to minimize poisoning will be an important aspect of metal oxide design for oxidation catalysis.

References

1. Hegedus, L.; McCabe, R., *Catal. Rev.*, 23, 377 (1981).
2. Assmann, J. et al., *J. Phys.: Condens. Matter* 20, 184017 (2008).
3. Lafosse, A.; Wang, Y.; Jacobi, K., *J. Chem. Phys.* 117, 2823 (2002).
4. Rossler, M.; Gunther, S.; Wintterlin, J., *J. Phys. Chem. C* 111, 2242 (2007).
5. Wang, H.; Schneider, W. F., *J. Chem. Phys*. 127, 064706 (2007).
6. Wang, Y.; Lafosse, A.; Jacobi, K. *J. Phys. Chem. B* 106, 5476 (2002).