Dissociative Adsorption of O2 on Clean and CO-Precovered Pt Surfaces

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ABSTRACT

It is generally accepted that CO oxidation on transition metals follows a Langmuir-Hinshelwood mechanism. The oxidation reaction takes place in two sequential steps where the oxygen molecule first dissociates into atomic oxygen and then reacts with an adsorbed CO to form CO_2. One critical question concerning the reaction kinetics under high pressure is the probability of oxygen dissociation on a highly CO covered surface. On bare transition metal surfaces, molecularly adsorbed oxygen readily dissociates with little or no apparent activation barrier. In industrial diesel engine catalysis, the metal surface is initially packed with CO. Subsequent reactions such as oxygen dissociation must take place on a CO covered surface. In this paper, we performed density functional theory (DFT) calculations for O_2 dissociation on Pt(111) in the presence of different CO adsorption environments. While several stable O_2 molecular precursor states (top-bridge-top, top-fcc-bridge, and top-hcp-bridge) exist on a clean Pt(111) surface, these precursors become endothermic beyond a critical CO coverage of ~0.44 ML. Furthermore, the reaction path for CO oxidation via dissociated atomic oxygen becomes less favorable at higher CO coverage, primarily due to competitive adsorption and lateral repulsion. It was found that the oxygen dissociation barrier and the binding energies of atomic oxygen are linearly correlated.

INTRODUCTION

The adsorption and dissociation of oxygen molecules plays an important role in the CO oxidation reaction on transition metal surfaces [1]. Even though oxygen dissociation on bare platinum metal surface proceeds with no apparent activation barrier, the situation is less clear on a CO covered surface [2]. There are many experimental and theoretical studies of oxygen dissociation reactions on platinum, where both molecular and atomic oxygen adsorption states have been observed [refs].

In order to gain insight into the effects of surrounding CO molecules on the oxygen dissociation path on Pt(111), we have performed density functional theory (DFT) calculations [3] with the nudged elastic band (NEB) method to locate the transition states [4]. Based on our simulations, we propose that there is a general repulsive effect of adsorbed CO molecules on both the oxygen precursor state and the dissociated atomic oxygen state. The effective result of the CO presence thus makes the overall oxygen dissociation route energetically less favorable. Our calculations offer a new perspective on the CO oxidation reaction path; for a Pt(111) surface packed with CO molecules, oxygen adsorption and dissociation only takes place in regions where the local CO concentration is relatively low. Some alternative mechanism might be responsible for CO oxidation under very high CO coverage. These findings give useful insight into the CO oxidation mechanism under realistic diesel engine operating conditions.

COMPUTATIONAL METHODS

Self-consistent DFT Calculations was done with $p(4x4)$ three-layer slab geometry and with Revised Perdew-Burke-Ernzerhof (RPBE) general gradient correction for the exchange-correlation functional, which has been shown to give accurate values for adsorption energies of many molecular species [5]. The Vienna ab initio simulation package was used for the calculations [6]. The Kohn-Sham single electron wavefunction was expanded by plane waves with an energy cut off of 400eV to maintain a finite basis set. This cut off was shown to give good convergence for both the adsorption energies and activation barriers. The metal slab consists of three layers, with the bottom metal layer fixed at its crystallographic bulk lattice positions, and the rest of the atoms free to relax in all directions. A vacuum layer of 11 Å has been introduced to eliminate image interactions. We used a 2x2x1 k-point mesh. The geometry optimization was terminated when the force on each atom was less than 0.05 eV/Å. The adsorption energy is calculated using the following equation:

$$\Delta E_{ads} = E_{total} - E_{substrate} - E_{molecule}$$

The minimum energy reaction path for oxygen dissociation on clean/CO covered Pt(111) surface was obtained by standard nudged elastic band (NEB) method [4]. Six intermediate images were used to interpolate the reaction path between the fixed reactant state and product state. Once a minimum-energy path is converged, the activation barrier is readily calculated as $E_a = E_{TS} - E_{IS}$, where E_{TS} and E_{IS} refer to the binding energy of transition state and initial state, respectively.

To get a reasonable representation of the CO adsorption pattern given the adsorbed O_2, Monte-Carlo simulations in conjunction with a parameterized CO lateral interaction were used [7]. Lateral interactions excluded the metal sites that were directly associated with adsorbed O_2 molecule and equilibrated the CO molecules on other sites on a $p(4x4)$ Pt(111) surface. The lowest energy pattern was then used in the subsequent DFT calculations to elucidate the relationship between O_2 adsorption/dissociation and CO coverage.

RESULTS AND DISCUSSIONS

A general picture of the stability of molecular oxygen precursor and atomic oxygen as a function of CO coverage will be presented in the first part of this section. We then deal in more detail with the reaction path of oxygen dissociation in the presence of co-adsorbed CO molecules and explore the energetics of the reaction path. Finally, we discuss their potential implications in the context of diesel engine catalysis.

O_2 precursor state on clean Pt(111) surface

Both theoretical and experimental evidence indicates the existence of a molecular oxygen precursor state on a clean platinum surface. We have put O_2 molecules on the clean Pt(111) surface at different positions and with different orientations. After optimization, three stable O_2 precursor states were identified. Figure 1 shows the energetically stable adsorption geometries of those O_2 molecular precursors. Among the three possible configurations, the O_2 precursor with t-f-b adsorption geometry has the lowest adsorption energy of -0.38 eV. We will use this particular

O$_2$ adsorption geometry for the following discussion of CO coverage dependent oxygen dissociation. However, our findings should also hold for O$_2$ dissociation starting from other precursor geometries.

(a)   t-fcc-b -0.37 eV   (b)   t-hcp-b -0.34 eV   (c)   t-b-t -0.30eV
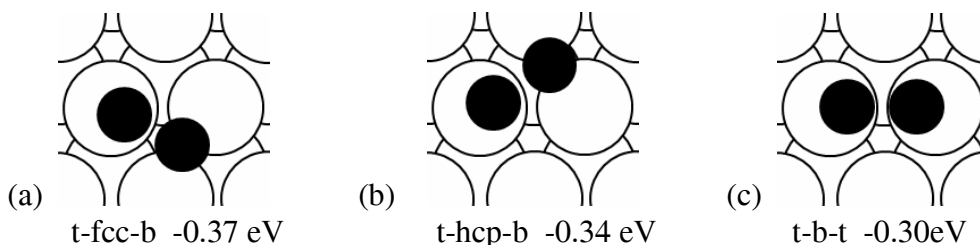
Figure 1. Stable adsorption geometries of O$_2$ molecule on a clean Pt(111) surface. a) t-fcc-b. b) t-hcp-b. c) t-b-t.

O$_2$ precursor state with CO coverage

We studied the O$_2$ precursor state under CO coverages of 0, 0.25, 0.31, and 0.44 ML, respectively. This corresponds to 0, 4, 5, 7 CO molecules in the p(4x4) unit cell. The adsorption patterns of co-adsorbed O$_2$ and CO obtained from the Monte-Carlo are shown in Figure 2. The details of the Monte-Carlo simulations can be found elsewhere [7]. Due to the repulsive interactions between CO molecules and CO-O$_2$ molecules, CO tends to form a relatively uniform distribution instead of forming islands or clusters on the surface.

(a) Clean   (b) 0.25 ML   (c) 0.31 ML   (d) 0.44 ML
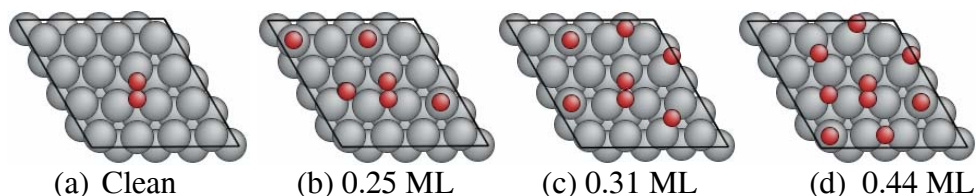
Figure 2. O$_2$ precursor states with differing amounts of CO coverage.

Column two and three of Table I list the adsorption energies of CO and O$_2$ at the same fcc site. It can be seen from the table that as we increase the CO coverage, both the CO adsorption energy and O$_2$ precursor energy decreased. These energies correlate linearly with each other with a slope of 1.33 and $R^2 = 0.99$, which indicates that surrounding CO has a slightly stronger influence on the adsorption of O$_2$ than the adsorption of CO. Figure 5a shows this linear relationship.

## O$_2$ dissociation barrier with CO coverage

We show in this section the path for the O$_2$ molecular precursor to dissociate into two atomic oxygens, occupying two neighboring fcc sites. Since the dissociated atomic oxygens share a metal atom, the total adsorption energy is less than the sum that is obtained for two atomic oxygens separated, which is -2.20 eV on Pt(111). The surrounding CO tends to destabilize the dissociated atomic oxygen even more.

We illustrate the reaction by considering the O_2 dissociation path on clean Pt(111) surface. All other reaction paths with CO coverage follow similar routes, except the detailed energetic and transition state geometries are slightly different. The dissociation of the t-fcc-b O_2 precursor state into two atomic oxygen involves the breaking of the O-O bond, while one atomic oxygen simultaneously migrate towards an fcc site via an atop site and the other oxygen remains almost on the bridge site during the transition state (figure 3). The detailed geometry of the transition state is shown in figure 4b for the clean surface case and some key parameters including the O-O and O-Pt bond lengths are listed on the last column of table I.

Table I. Adsorption energies and geometries of CO*, O_2* and O*

Pt(111)	CO* (eV)	O_2* (eV)	2O* (eV)	TS (eV)	Geometries of TS (Å)	
					O-O	O-Pt[a]
Clean	-1.51	-0.38	-1.94	-0.13	2.28	1.83(T) 1.98(B) 1.98(B)
0.25ML	-1.35	-0.20	-1.59	+0.05	2.10	1.85(T) 2.01(B) 2.01(B)
0.31ML	-1.32	-0.14	-1.26	+0.17	2.23	1.83(T) 1.99(B) 2.00(B)
0.44ML	-1.21	+0.02	-0.91	+0.41	2.03	1.86(T) 2.04(B) 2.00(B)

a) the T/B in the parenthesis Pt bonds to either an atop (T) oxygen or bridge (B) oxygen.

Side View

Top View

      t-fcc-b   Img 01   Img 02(TS) Img 03   Img 04   Img 05   Img 06   fcc-fcc
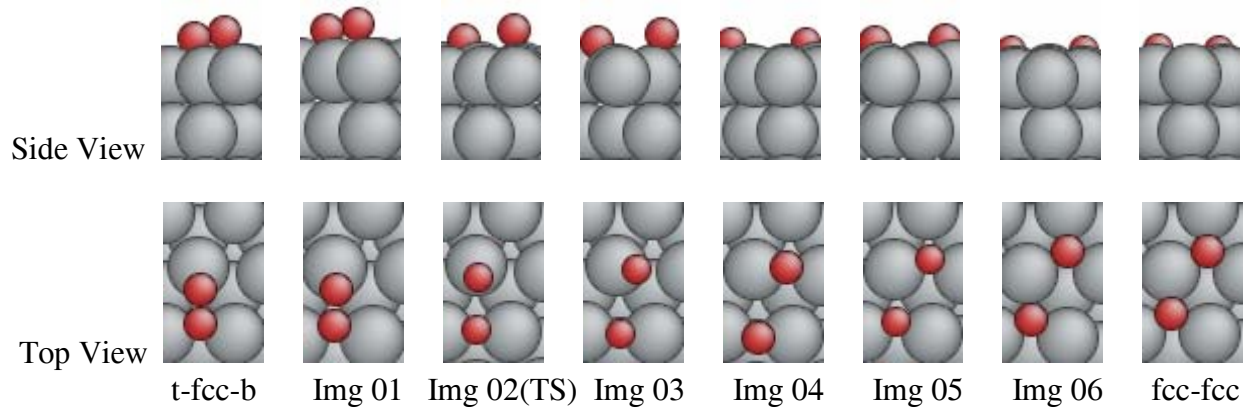
Figure 3. The side-view and top-view of the O_2 dissociation reaction path on Pt(111). The details of the transition state geometry are reported in table 1.

In figure 4, we show the dependence of energies of the O_2 precursor state, transition state, and final state as a function of CO coverage. The O_2 molecular precursor state is initially stable with adsorption energy of -0.37 eV and there is no apparent activation barrier for O_2 dissociation. As we gradually increase the CO coverage; the precursor state energy rises with respect to O_2 in the gas phase and finally becomes endothermic when CO coverage reaches 0.44 ML. The

transition state energy and final state energy follow similar trends, except that the change in those energies is even more pronounced with increasing CO coverage. Figure 5b shows the linear correlation between the transition state energy and the O_2 precursor energy. A similar relationship has also been found for the elementary CO oxidation step, where the reaction barriers are mainly determined by the initial state energies [8,9]. The overall reaction barrier for CO oxidation is influenced by both the CO desorption energy and the oxygen dissociation activation barrier. Our calculations indicate that as CO continues packing the surface, there is a critical coverage beyond which the rate limiting step of CO oxidation changes from CO desorption to O_2 activation.
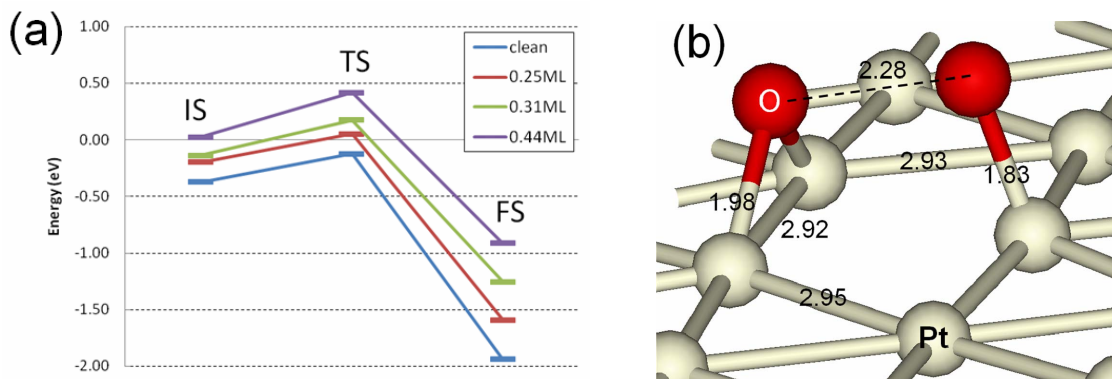
Figure 4. a) O_2 dissociation energy as a function of CO coverage. b) detailed transition state geometry of O_2 dissociation on clean Pt(111) surface.
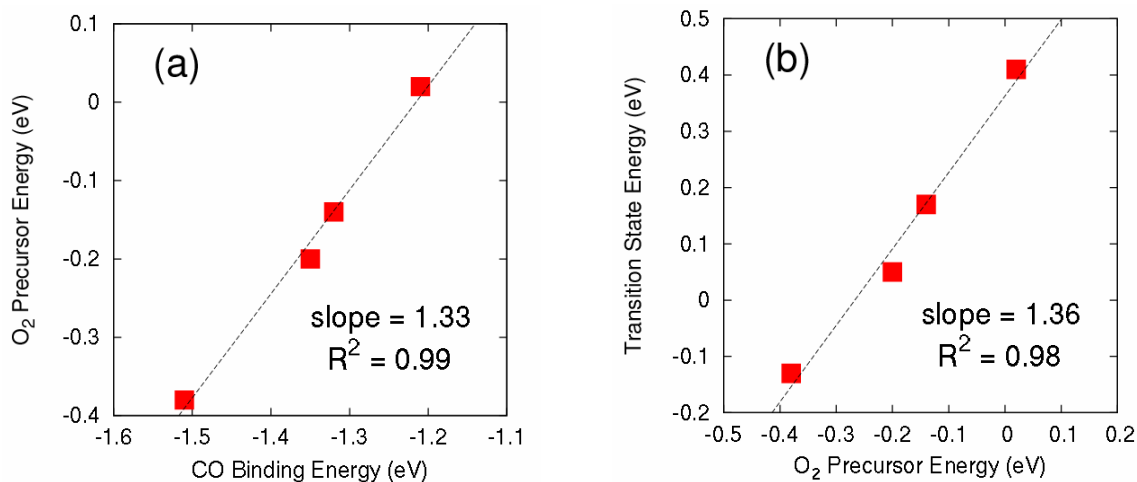
Figure 5. a) Correlation between CO adsorption energy and O_2 precursor energy. b) Linear relationship between transition state energy and precursor adsorption energy

Other possible reaction paths

From the above analysis, it can be seen that O_2 dissociation barrier is a strong function of CO coverage. Under high CO coverage conditions, the O_2 dissociation becomes less favorable. We have examined the extreme case where CO coverage is 0.75 ML. The calculated O_2 dissociation is larger than 1.5 eV. This is not consistent with the experimentally observed

apparent activation barrier under high CO coverage. A number of experiments have already shown that CO oxidation under high coverage might not obey a Langmuir-Hinshelwood mechanism. It is possible that under high CO coverage conditions, the CO oxidation goes under alternative route which does not involve a direct O_2 dissociation, but through an O_2 molecule directly reacting with adsorbed CO. Another possibility is that O_2 dissociation takes place in the vicinity of defects where vacant sites are more available.

CONCLUSIONS

The reaction path of O_2 dissociation on Pt(111) surface under different CO coverage conditions has been studied using periodic self-consistent DFT (GGA-RPBE) calculations. Despite the barrierless oxygen dissociation on a clean Pt surface, the reaction path shows a considerable barrier when CO are present on the surface. Both the O_2 precursor state and transition state show good correlation to the CO adsorption on that site, but with a stronger dependence to CO coverage. The binding of the oxygen molecular precursor changes from exothermic to endothermic at around 0.44 ML CO coverage, beyond which oxygen dissociation becomes more and more difficult. O_2 dissociation becomes very unlikely under very high CO coverages. Our study gives useful insight into the effect of CO molecules on the O_2 dissociation and their potential implications in influencing the overall reaction kinetics.

ACKNOWLEDGMENTS

REFERENCES

1. A. Eichler, F. Mittendorfer, and J. Hafner, *Phys. Rev. B* **62**, 4744 (2000)
2. Z. Sljivancanin, and B. Hammer, *Surf. Sci.* **515**, 235 (2002).
3. W. Kohn, *Rev. Mod. Phys.* **71**, 1253 (1999).
4. H. Jonsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), p. 385.
5. B. Hammer, L. B. Hansen, and J. K. Norskov, *Phys. Rev. B* **59**, 7413 (1999).
6. G. Kresse, J. Furthemuller, *Comp. Mat. Sci.* **6**, 15 (1996).
7. B. Shan, L. Wang , J. Hyun, S. Yang, Y. Zhao, and J.B. Nicholas, *MRS proceedings*, San Francisco, CA (2008).
8. Z. P. Liu and P. Hu, Topics in Catal. **28**, 71 (2004).
9. Z. P. Liu and P. Hu, J. Chem. Phys. **115**, 4977 (2001).