

General Insight into CO Oxidation: A Density Functional Theory Study of the Reaction Mechanism on Platinum Oxides

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CO oxidation on PtO₂(110) has been studied using density functional theory calculations. Four possible reaction mechanisms were investigated and the most feasible one is the following: (i) the O at the bridge site of PtO₂(110) reacts with CO on the coordinatively unsaturated site (CUS) with a negligible barrier; (ii) O₂ adsorbs on the bridge site and then interacts with CO on the CUS to form an OO-CO complex; (iii) the bond of O-OCO breaks to produce CO₂ with a small barrier (0.01 eV). The CO oxidation mechanisms on metals and metal oxides are rationalized by a simple model: The O-surface bonding determines the reactivity on surfaces; it also determines whether the atomic or molecular mechanism is preferred. The reactivity on metal oxides is further found to be related to the 3rd ionization energy of the metal atom.

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Because of its industrial and theoretical importance, CO oxidation on transition metal surfaces is regarded as the prototype reaction in heterogeneous catalysis and has been widely studied [1–4]. Recently, CO oxidation on transition metal oxides has also attracted particular attention. Despite progress made in the area, many aspects of the reaction mechanism are largely elusive. In this Letter, we investigate the CO oxidation mechanisms on Pt oxides to identify a low energy pathway. Perhaps more importantly, we intend to shed some light on CO oxidation mechanisms and reactivity on metals and metal oxides in general.

It is known that some transition metals, such as Pt and Pd, are good catalysts for CO oxidation [5]. However, recently Ertl and co-workers found that some metal oxides could be active in CO oxidation too. In their pioneering work, they studied CO oxidation on ruthenium and ruthenium oxide surfaces [6–8]. They showed that the rate of CO oxidation on the ruthenium oxide [RuO₂(110)] formed on the metal surface [Ru(0001)] is much higher than that on Ru(0001). More recently, another breakthrough was made by Hendriksen and Frenken: by studying CO oxidation on Pt(110) in a high-pressure flow reactor, they demonstrated that higher O₂ partial pressure in the CO + O₂ mixed gas feed can significantly increase CO₂ formation rate [9]. They showed in their STM images that the surface might be oxidized in the oxygen-rich flow, and they proposed that the oxidized surface is catalytically much more active than Pt(110).

Considering that CUS-metal [CUS refers to the *coordinatively unsaturated site*, labeled in Fig. 1(a)] is the only free site for CO or O₂, the two CO oxidation mechanisms can be envisaged. Mechanism (a): CO(CUS) reacts with an O(bridge) to form CO₂, and O(bridge) atoms are supplied by O₂ dissociation on the bridge sites. Mechanism (b): CO adsorbs and O₂ dissociates on the CUS-metal to form CO(CUS) and O(CUS), respectively,

followed by their combination to produce CO₂. The first mechanism on RuO₂(110) was investigated by Liu, Hu, and Alavi using density functional theory (DFT) [10]. Recently, Reuter and Scheffler systematically studied the CO oxidation on RuO₂(110) and both mechanisms were thoroughly examined [11]. For mechanism (a) they obtained a barrier similar to that of Liu, Hu, and Alavi, while for mechanism (b) they calculated the barrier to be around only 0.8 eV, indicating that this could be the key reaction for low-temperature CO oxidation on RuO₂(110).

Although significant progress has been made regarding CO oxidation on metal oxides [8–12], it is still not clear whether mechanism (b) is a general one. In particular, the mechanism of CO oxidation on platinum oxides has not been well investigated. In this work, we examined almost all possible CO oxidation mechanisms on PtO₂(110) and then compared them to those in other systems, aiming to obtain a simple, yet general, framework for CO oxidation on metals and metal oxides.

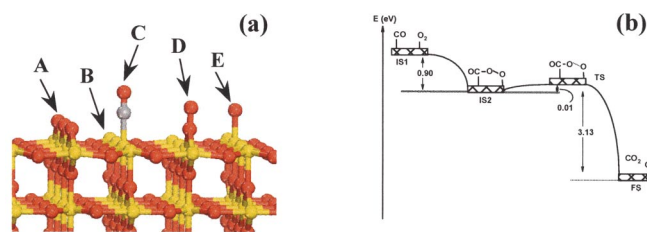


FIG. 1 (color online). (a) The different sites and adsorbates on PtO₂(110). A, O(bridge); B, CUS-Pt; C, CO(CUS); D, O₂(bridge); E, O(CUS). (b) The energy profile of reaction CO(CUS) + O₂(bridge) → [CO(CUS) – O₂(bridge)]_{complex} → CO₂(gas) + O(bridge) on PtO₂(110). IS1 and IS2 are the systems with coadsorbed CO(CUS)/O₂(bridge) and [CO(CUS) – O₂(bridge)] complex on PtO₂(110), respectively. TS and FS are the transition state of CO₂ formation and the final state of this reaction with CO₂ in gas phase and O(bridge) on the surface.

The total energy calculations were performed using the DFT-slab approach with generalized gradients approximation of Perdew-Burke-Ernzerhof functional and plane wave basis set [13(a)]. Ultrasoft pseudopotentials were used to describe the ionic cores [13(b)]. Considering that PtO_2 is a stable oxide and $\text{PtO}_2(110)$ is the most stable surface, and also the fact that $\text{RuO}_2(110)$ is active for CO oxidation, we selected $\text{PtO}_2(110)$ as the catalyst to model CO oxidation on Pt oxides. It should be noted that under real reaction conditions [9] the catalyst may not be exactly the structure modeled here, but we believe that our model calculations should provide a correct trend and the understanding obtained should be useful. The $\text{PtO}_2(110)$ surface is modeled by nine layers of metal oxides, and the top four layers are relaxed. The $p(2 \times 1)$ and $p(3 \times 1)$ unit cells were utilized corresponding to different reactions, and the Monkhorst Pack meshes of $3 \times 3 \times 1$ and $2 \times 3 \times 1$ k -point sampling in the surface Brillouin zone were used for them, respectively. The same settings were also used on other oxide surfaces [12]. In the calculations performed on metals, the surfaces were modeled by four layers of metals with the first layer relaxed. The $p(2 \times 2)$ unit cell and $3 \times 3 \times 1$ k -point sampling were used. The vacuum region between slabs was ~ 10 Å, and a cutoff energy of 350 eV was used. Our previous work shows that the above settings are accurate enough to give rise to the correct reactivity trend. The transition states (TSs) were searched using a constrained optimization scheme as described before [14–16].

First of all, we examined the possibility of CO oxidation through mechanisms (a) and (b) on $\text{PtO}_2(110)$. For mechanism (a), we found that the $\text{CO}(\text{CUS})$ can readily react with the $\text{O}(\text{bridge})$ and the barrier is negligible. The TS structural parameters are listed in Table I. However, the barrier of O_2 dissociation on the bridge site is too high (over 2 eV) with respect to the initial state (IS) of O_2 adsorbed on the bridge site. Therefore, the O supply is hindered, and this atomic mechanism is not feasible on $\text{PtO}_2(110)$. For mechanism (b), it was found that O_2 dissociation on CUS-Pt atoms is not favored thermodynamically because our calculations show the final state (FS) of the dissociation is about 1.5 eV less stable than the IS with the O_2 molecule in the gas phase.

TABLE I. The important structural parameters in the transition states. Reaction 1 is the reaction between $\text{CO}(\text{CUS})$ and one $\text{O}(\text{bridge})$ on $\text{PtO}_2(110)$ in a $p(2 \times 1)$ unit cell. Reaction 2 is the reaction between $\text{CO}(\text{CUS})$ and $\text{O}_2(\text{bridge})$ on $\text{PtO}_2(110)$ at high O_2 coverages. O^* is the reacting O, O^\S is the O in CO, and $\text{O}^\#$ is the nonreacting O in $\text{O}_2(\text{bridge})$.

Distance Å	Reaction 1	Reaction 2
C- O^*	2.014	1.322
C- O^\S	1.154	1.209
$\text{O}^*-\text{O}^\#$...	1.760

After ruling out the two atomic mechanisms on $\text{PtO}_2(110)$, we investigated two mechanisms involving the O_2 molecule. Mechanism (c): $\text{CO}(\text{CUS}) + \text{O}_2(\text{CUS}) \rightarrow \text{CO}_2 + \text{O}(\text{CUS})$, $\text{CO}(\text{CUS}) + \text{O}(\text{CUS}) \rightarrow \text{CO}_2$; mechanism (d): $\text{CO}(\text{CUS}) + \text{O}_2(\text{bridge}) \rightarrow \text{CO}_2 + \text{O}(\text{bridge})$, $\text{CO}(\text{CUS}) + \text{O}(\text{bridge}) \rightarrow \text{CO}_2$. In the calculation on the reaction directly between CO and O_2 molecules on CUS sites [mechanism (c)], we used the $p(3 \times 1)$ unit cell in order to avoid the interaction between the reactants in neighboring unit cells. We found that the $\text{CO}(\text{CUS})$ and the $\text{O}_2(\text{CUS})$ molecule can form an $\text{OC}-\text{O}_2$ complex. Compared to the system with O_2 in the gas phase, the complex state is 0.61 eV more stable. We also located the TS leading to the formation of CO_2 and the calculated barrier is 0.67 eV. However, this barrier is higher than the chemisorption energy of O_2 in the complex (0.61 eV), indicating that the complex decomposition, which leads to the O_2 desorption, is more favored than the CO_2 formation. Therefore, CO oxidation through mechanism (c) is also not favored.

Then, we investigated mechanism (d). As mentioned above, the $\text{O}(\text{bridge})$ on $\text{PtO}_2(110)$ can be easily removed through $\text{CO}(\text{CUS}) + \text{O}(\text{bridge}) \rightarrow \text{CO}_2$. After the $\text{O}(\text{bridge})$ atoms are removed, those bridge sites become available for further adsorption. Although both O_2 and CO can adsorb on bridge sites, we expect that the O_2 population on bridge sites is very high because the partial pressure of O_2 in the gas phase is much higher than that of CO [9]. We found that at moderate O_2 coverages (0.5 ML), the O_2 molecule can insert into the bridge site with the O-O bond along the $[001]$ direction. The calculated chemisorption energy is 1.65 eV. At high coverages (O_2 coverage = 1 ML), two upright O_2 molecules can adsorb on the neighboring bridge sites and the chemisorption energy for each O_2 is 0.86 eV.

Considering that the partial pressure of O_2 in the gas phase is high and thus the structure with high O_2 coverage is favored, we further studied the reaction of $\text{CO}(\text{CUS}) + \text{O}_2(\text{bridge})$ at high O_2 coverages. Once CO is on the CUS site, the $\text{CO}(\text{CUS})$ and the $\text{O}_2(\text{bridge})$ can tilt towards each other to form a complex with an energy gain of 0.90 eV. We also located the TS for CO_2 formation and the important structural parameters of the TS are listed in Table I. As can be seen from Table I, the distance between the C and the reacting O is 1.322 Å, and the distance between the reacting O and the other O remaining on the bridge site is stretched to 1.760 Å. The calculated barrier is only 0.01 eV. After this reaction, the O atom left on the bridge site can readily react with another $\text{CO}(\text{CUS})$ as mentioned above. The profile depicting the total energy change along this reaction route is shown in Fig. 1(b), indicating that this mechanism is feasible. It may also explain why the activity of Pt(110) to CO oxidation is significantly increased after being oxidized.

One may wonder why the O_2 is so reactive on $PtO_2(110)$. A recent DFT study from our group showed that in the $Au/TiO_2(110)$ system [Au strip supported on $TiO_2(110)$], the CO oxidation through $CO + O_2$ combination can occur at the metal/oxide interface with the barrier as low as 0.1 eV [17], which is very close to the small barrier obtained in the current work. Also similar to the result in this work, the chemisorption energy of the reacting O_2 at the Au/TiO_2 interface is reasonably high (0.86 eV) [17]. In fact, we believe that the presence of O_2 molecules on the catalytic surface with a reasonable chemisorption energy is the key factor to the molecular mechanism for CO oxidation. First, the reasonably high chemisorption energy can increase both the coverage of O_2 on the surface and the chance for it to react with CO. Second, it can activate the O_2 molecule and reduce the reaction barrier. The second point can be understood as follows. According to our calculations, the Mulliken charge of the reacting O_2 molecule in the CO/ O_2 coadsorption system on $PtO_2(110)$, which is the IS of $CO_2 + O_2 \rightarrow CO_2 + O$ reaction [IS] in Fig. 1(b), is -0.62 , indicating a considerable amount of charge transfer from the surface to the O_2 . As pointed out in our previous paper, the charge is in the O_2 antibonding orbital (2π) [17], which will significantly weaken the O-O bond, leading to the activation of O_2 and the low barrier of CO + O_2 reaction.

It is interesting to note that the atomic mechanism, in which CO_2 is produced through $CO + O$, is the dominating one on metal surfaces, e.g., Pt, Pd, and Rh, and is also feasible on some metal oxides, such as $RuO_2(110)$ [4,8,18,19]. On the other hand, the molecular mechanism ($CO + O_2 \rightarrow CO_2 + O$) is favored on $PtO_2(110)$ and $Au/TiO_2(110)$. Can these results be rationalized within

a simple framework? The answer to this question can be found in Fig. 2, in which the O chemisorption energy with respect to O_2 in the gas phase on some $4d$ and $5d$ metal surfaces and corresponding metal oxides are plotted [note that, except for $Ru(0001)$ and $Os(0001)$, the (111) and (110) surfaces were used for pure metals and metal oxides, respectively]. The data are listed in Table II. In region I, the molecular mechanism is preferred because O_2 dissociation is not favored thermodynamically. In region II, the O_2 can dissociate and thus the atomic mechanism is feasible. Furthermore, the reactivity of CO oxidation in these systems can be generalized: In a recent work, Nørskov and co-workers proposed the presence of the universal relation between the activity of a surface and the bonding energy of reactants on the surface [20]. They suggested that only those catalysts, on which the bonding energies of reactants are within a narrow window, are active. This excellent work can be extended here. Below region II, the O-surface bonding is too strong, and, therefore, the CO oxidation barrier will be large [12,21]. Above region I, the O-surface bonding is too weak and thus it is expected that O_2 chemisorption is not strong. Therefore, the O_2 coverage will be low, and, more importantly, the O_2 is not activated, which would not result in an efficient CO oxidation through the molecular mechanism, as discussed above. It should be mentioned that the boundaries of regions I and II may not be exact as shown in the figure. However, Fig. 2 not only indicates the relative activity of those surfaces but also suggests which mechanism may be favored. For example, it is known that $Ru(0001)$ is not a good catalyst for CO oxidation. Therefore, it may not be surprising that $Os(0001)$ is not good either, because the chemisorption energies of O on both surfaces are similar. Being consistent with experiments, Fig. 2 shows that $RuO_2(110)$ is a better catalyst for CO oxidation than $Ru(0001)$. It also indicates that $OsO_2(110)$ may not be as good as $RuO_2(110)$. As another special example, O chemisorption on Au lands in region I in the figure, indicating the preference of molecular mechanism in the system, which is consistent with other previous work [17,22].

In fact, we also found the following two striking features in Fig. 2 regarding the reactivity of metal oxides: First, O chemisorption on both $4d$ and $5d$ metal oxides decreases as the atomic number increases. Second, the O

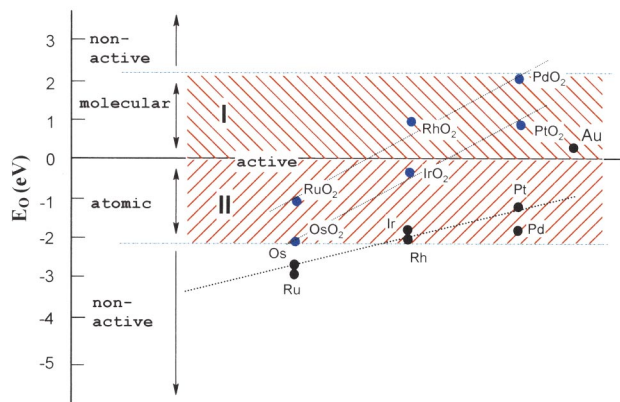


FIG. 2 (color online). Calculated O chemisorption energies (E_0) with respect to O_2 in the gas phase on some $4d$ and $5d$ metals and metal oxides. The data are shown in Table II. The O is on the fcc hollow site on $Ir(111)$, $Rh(111)$, $Pt(111)$, and $Pd(111)$, and on the hcp hollow site on $Os(0001)$ and $Ru(0001)$. The O on the $MO_2(110)$ surfaces ($M = Ru, Os, Rh, Ir, Pd, \text{ and } Pt$) are on the CUS site.

TABLE II. The calculated O chemisorption energy on metals and metal oxides with respect to the O_2 in the gas phase, and the 3rd ionization energy of the metal atoms.

	Ru	Rh	Pd	Os	Ir	Pt
E_0 (eV)	-2.86	-1.98	-1.78	-2.63	-1.76	-1.18
3rd E_{ion} (eV)	28.66	30.01	32.55	27.06	28.56	30.57
	RuO_2	RhO_2	PdO_2	OsO_2	IrO_2	PtO_2
E_0 (eV)	-1.00	1.00	2.06	-2.08	-0.35	0.92

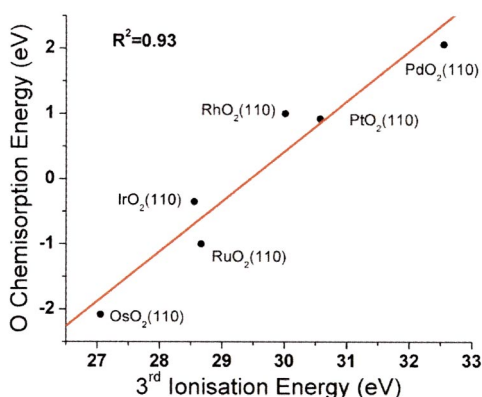


FIG. 3 (color online). O chemisorption energy on the metal oxide (E_0 , see Fig. 2 and Table II) as a function of the 3rd ionization energy of the corresponding metal atom. The data are also listed in Table II.

chemisorption on 4d metal oxides is significantly weaker than the corresponding 5d metal oxides, in contrast to the fact that the O-4d metal bonding is similar to (or slightly stronger than) that on 5d metals. For example, the O chemisorption energy on RuO₂(110) is around 1 eV higher than that on OsO₂(110), while on Ru(0001) and Os(0001) the difference is around only 0.2 eV (Table II).

In order to find the physical origin of these trends, which is crucial to understanding the relative reactivity of metal oxides, we calculated the ionization energies of all the six metal atoms. After careful examination of the results, we found that there is a strong correlation between the O chemisorption energies on the metal oxides and the calculated 3rd ionization energies of the corresponding metals, as shown in Fig. 3. It can be seen that the larger the 3rd ionization energy, the weaker the O chemisorption. It is clear that the activity trends from both 4d and 5d metal oxides reported above can be described by *one* property: ionization energy. This is consistent with conventional chemistry; the CUS-metal atom has a charge close to +3, and the O-CUS-metal bonding is mainly ionic. This means that there is a charge transfer from the CUS-metal atom to the O atom when the O adsorbs on the surface. Therefore, it is not surprising that the higher the 3rd ionization energy, the more difficult it is for the CUS-metal to lose electrons to the O, and the weaker the O chemisorption. This implies that we may use ionization energies to estimate the activity of metal oxides.

In summary, our DFT calculations suggest that CO oxidation on platinum oxides follows the molecular mechanism and can proceed with very low barriers. Our results also shed some light on CO oxidation on both metals and metal oxides. The reactivity and, perhaps more importantly, the reaction mechanisms are generalized within a simple framework. In addition, the relative reactivity on metal oxides is found to be determined by a

single property—the 3rd ionization energy. It is worth reiterating that the above trends and understanding were obtained from typical metal oxide structures. Further studies of the reaction on other oxide structures would be of great interest.

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