A Systematic Study of CO Oxidation on Metals and Metal Oxides: Density Functional Theory Calculations

Xue-Qing Gong,[†] Zhi-Pan Liu,[†] Rasmita Raval,[‡] and P. Hu*,[†]

School of Chemistry, The Queen's University of Belfast, Belfast, BT9 5AG, U.K., and Surface Science Research Centre, The University of Liverpool, Liverpool, L7 3BX, U.K.

Received June 30, 2003; Revised Manuscript Received October 27, 2003; E-mail: p.hu@qub.ac.uk

Metal and metal oxide surfaces are the most common surfaces on which reactions occur in heterogeneous catalysis. Thus, to understand the reactivity of these surfaces and the differences between them is of paramount importance. Our concern here is to obtain such an understanding from CO oxidation.

CO oxidation is often used as a model system to understand catalysis due to its simplicity. Since the pioneering work of Langmuir,[1] CO oxidation under both real and ultrahigh vacuum (UHV) conditions has been extensively studied.[2−5] Recently, some excellent experimental works have provided new insight into this reaction.[6−12] Using several techniques, Ertl and co-workers have obtained strong evidence for a new mechanism for CO oxidation on Ru(0001), that under O_2-rich conditions and moderate temperatures, Ru(0001) is first oxidized into RuO_2(110) and CO oxidation actually occurs on RuO_2(110).[10] More recently, Hendriksen and Frenken carried out a study of CO oxidation on Pt(110) in a high-pressure flow reactor.[11] They demonstrated that the oxidized Pt surface is more reactive than pure Pt for CO oxidation. Very recently, Reuter and Scheffler carried out a detailed DFT study of CO oxidation on RuO_2(110).[13a] They examined two reaction pathways: (i) the chemisorbed CO (cus-CO) reacts with a lattice bridge-O (see Figure 1), and (ii) the cus-CO reacts with an adsorbed O atom on a cus-Ru atom (cus-O) (see Figure 1). They found that the first reaction barrier is high, similar to that obtained by Liu, Hu, and Alavi,[14] while the second barrier, 0.89 eV,[13a] is much lower than that on Ru(0001),[13b] which is consistent with the experimental findings and thus appears to be the pathway for CO oxidation on RuO_2(110).

Although a new mechanism for CO oxidation has been identified by both experimental and theoretical works, there are still two fundamental issues remaining to be tackled: (i) Is it generally true that the activity of metal oxide is higher than that of the corresponding metal for CO oxidation? (ii) If the answer is yes, what is the origin of the activity increase from metals to metal oxides? Aiming to answer these two questions in this work, we systematically studied CO oxidation on Ru(0001), Rh(111), Pd-(111), Os(0001), Ir(111), Pt(111), and their corresponding metal oxides (RuO_2(110), RhO_2(110), PdO_2(110), OsO_2(110), IrO_2(110), and PtO_2(110)). It should be noted that some structures of the oxides may not be ones in real catalysis: The structure of Pd oxide has not been well defined experimentally. However, this will not affect the main purpose of this work, identifying general reactivity trends on the metals and their metal oxides.

In this study, total energy calculations using the DFT-slab approach with GGA-PBE functional and plane wave basis set were performed.[15a] Ultrasoft pseudopotentials were used to describe the ionic cores.[15b] The surfaces were modeled by four layers of metals and nine layers of metal oxides (details in ref 16).

[†] The Queen's University of Belfast.
[‡] The University of Liverpool.
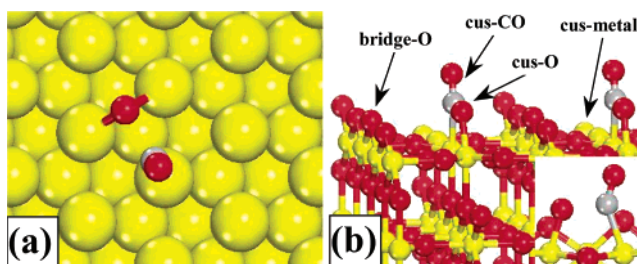
Figure 1. The geometrical structures of TSs of CO + O → CO_2 on metals and metal oxides. The yellow ball represents the metal atom, the gray ball represents C, and the red ball represents O. (a) Top view of the structure of the TS on metals (Rh, Pd, Ir, Pt) (on Ru and Os, the bonds of O−CO are over the fcc hollow sites). (b) Side view of the structure of the TS on metal oxides (inset: a different view of the TS on the metal oxides).

Table 1. Calculated Reaction Barriers of CO + O → CO_2 on Metals and Metal Oxides[a]

	4d		
metal	Ru(0001)	Rh(111)	Pd(111)
barrier (eV)	1.68	1.17	0.91
R-barrier (eV)	0.95	0.71	0.30
OC−O distance (Å)	1.75	1.84	1.90
metal oxide	RuO_2(110)	RhO_2(110)	PdO_2(110)
barrier (eV)	0.66	0.22	0.03
OC−O distance (Å)	1.80	2.07	2.46
	5d		
metal	Os(0001)	Ir(111)	Pt(111)
barrier (eV)	1.71	1.29	0.79
R-barrier (eV)	0.80	0.59	0.09
OC−O distance (Å)	1.77	1.84	2.02
metal oxide	OsO_2(110)	IrO_2(110)	PtO_2(110)
barrier (eV)	1.18	0.61	0.05
OC−O distance (Å)	1.71	1.85	2.44

[a] R-barrier refers to the reduced barrier as defined in the text. OC−O distances are the bond lengths at the TSs.

First, we determined the most stable initial state (IS) for the CO + O coadsorption system on each surface. On all of the metal surfaces, the ISs are similar: CO is on the top site and O is on either the fcc hollow site (Rh, Pd, Ir, Pt) or the hcp hollow site (Ru, Os). Similarly, the ISs on the metal oxides are also alike, with our calculations showing that the top site of cus-M atom (M = Ru, Rh, Pd, Os, Ir, and Pt) is favored by both CO and O. We then located the TS for CO + O reaction on each surface. We found that all of the TSs on the metal surfaces are alike (Figure 1a) and all of the metal oxides possess similar TSs (Figure 1b), too. The important structural parameters of the TSs are listed in Table 1. The reaction barriers are also listed in the table. It shows clearly that the barrier on each metal oxide is significantly lower than that on the corresponding metal surface. These results indicate that in general the metal oxides are indeed more reactive than their
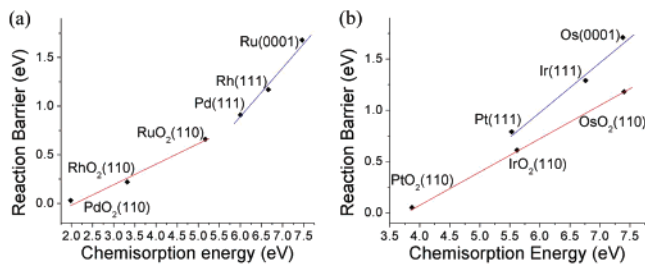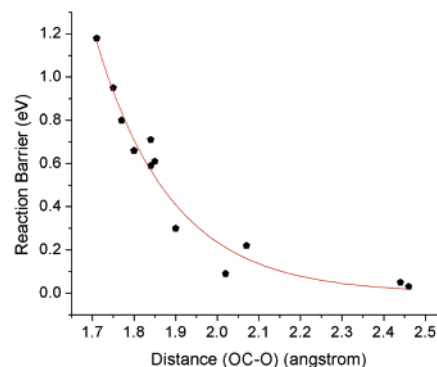
Figure 2. Reaction barrier as a function of the total chemisorption energy (CO and O) in the IS for 4d metals and their oxides (a), and 5d metals and their oxides (b).

corresponding metals for CO oxidation. The calculated results on Ru and Pt are also consistent with recent experimental observations.[10,11]

To understand these results, we carried out detailed analyses. First, we found that there is a relationship between the total chemisorption energy of CO and O in the IS and the barrier, as shown in Figure 2 (4d metals and metal oxides in Figure 2a and 5d metals and metal oxides in Figure 2b). It can be seen that the stronger the chemisorption is in the IS, the higher the barrier. Therefore, one may expect that the increased reactivity of metal oxides as compared to their corresponding metals is simply due to the fact that the CO and O bond less strongly on the oxide than on the metal. However, this explanation is not complete; the total chemisorption energy of the IS on $OsO_2(110)$ is slightly higher than that on $Os(0001)$, but the barrier on $OsO_2(110)$ is still much lower. Careful examination of the IS and the TS structures reveals that there is an additional reason (maybe more fundamental) for the high reactivity of metal oxides. From Figure 1, one can see that on metal oxides the O atom is on the top site of a cus-metal atom in the IS, and it is still close to the top site in TS. However, this is not the case on the metal surfaces; in the IS, the O atom is on the hollow site, while it is activated from the hollow site to the bridge site in the TS. This means that an extra energy cost, the activation for the O atom to move from the hollow site to the bridge site, is counted in the barrier on the metal surfaces as compared to that on the metal oxides. Indeed, if we decompose the CO oxidation on metals into two steps, (i) the O atom moves from the hollow site to the bridge site, and (ii) the CO and the O move together to achieve the TS, the energy cost from the second step, the so-called reduced barrier in Table 1, is then comparable to the barrier on the corresponding metal oxide. Therefore, we suggest that the geometric effect of metal oxides, on which the TS is allowed to be achieved without a significant O movement, plays an important role in reducing the barrier.

As discussed above, both the chemisorption energy of reactants, which can be classified as the electronic effect, and the geometric effect can affect the barrier. To further examine the electronic effect on the barrier, we used the reduced barrier for metals to exclude the geometric effect. We identified a good relationship between the barriers of reactions and their TS geometries (Figure 3): the shorter the OC−O bond distance is at the TS, the higher the barrier. The result shows interestingly that the electronic effect in CO oxidation on both metals and metal oxides follows the same pattern. Our understanding of this general correlation is the following: The TS is such a state that all of the forces are zero. It can be approximately considered that the force along the OC−O bond at the TS is balanced by the forces from the OC−metal bond and the O−metal bond. If the OC−metal and the O−metal bonding are then strong in a system, the OC−O bond has to be strong as well at the TS, which can only be achieved by shortening the bond

Figure 3. Reaction barrier as a function of the OC−O distance in the TS. The solid line is a first-order exponential decay curve with R^2 being 0.96.

distance of OC−O. Therefore, the stronger the OC−metal and the O−metal bonding, the shorter the OC−O distance, and the higher the barrier is.

In summary, this work represents a systematic theoretical study of CO oxidation on metals and metal oxides. We show that the barriers on metal oxides are generally lower than their corresponding metals for CO oxidation and the higher activity of metal oxides is attributed mainly to the surface geometric effect. We also illustrate that the barriers from both metal oxides and metals (reduced barriers) follow a general pattern: the shorter the OC−O bond distance is at the TS, the higher the barrier. Finally, it should be emphasized that metal oxides may well form in other reactions under elevated pressure conditions.[19,20] Thus, the results reported here are of general significance, not only for CO oxidation but also for other reactions.

References
(1) Langmuir, I. *Trans. Faraday Soc.* **1921**, *17*, 621.
(2) Ertl, G. *Surf. Sci.* **1994**, *299*, 742.
(3) Stampfl, C.; Scheffler, M. *Phys. Rev. Lett.* **1997**, *78*, 1500.
(4) Yeo, Y. Y.; King, D. A. *J. Chem. Phys.* **1997**, *106*, 392.
(5) Alavi, A.; Hu, P.; Deutsch, T.; Silvestrelli, P. L.; Hutter, J. *Phys. Rev. Lett.* **1998**, *80*, 3650.
(6) Böttcher, A.; Conrad, H.; Niehus, H. *Surf. Sci.* **2000**, *452*, 125.
(7) Wang, J.; Fan, C. Y.; Jacobi, K.; Ertl, G. *Surf. Sci.* **2001**, *481*, 113.
(8) Fan, C. Y.; Wang, J.; Jacobi, K.; Ertl, G. *J. Chem. Phys.* **2001**, *114*, 10058.
(9) Böttcher, A.; Niehus, H.; Schwegmann, S.; Over, H.; Ertl, G. *J. Phys. Chem. B* **1997**, *101*, 11185.
(10) Over, H.; Kim, Y. D.; Seitsonen, A. P.; Wendt, S.; Lundgren, E.; Schmid, M.; Varga, P.; Morgante, A.; Ertl, G. *Science* **2000**, *287*, 1474.
(11) Hendriksen, B. L. M.; Frenken, J. W. M. *Phys. Rev. Lett.* **2002**, *89*, 046101.
(12) Daniell, W.; Weingand, T.; Knozinger, H. *J. Mol. Catal. A: Chem.* **2003**, *204*, 519.
(13) (a) Reuter, K.; Scheffler, M. *Phys. Rev. Lett.* **2003**, *90*, 046103; *Phys. Rev. B* **2003**, *68*, 045407. (b) Stampfl, C.; Scheffler, M. *Surf. Sci.* **1999**, *433−435*, 119.
(14) Liu, Z.-P.; Hu, P.; Alavi, A. *J. Chem. Phys.* **2001**, *114*, 5956.
(15) (a) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671. (b) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.
(16) The top one and the top four layers are relaxed on metals and metal oxides, respectively. To be consistent, the p(2 × 2) unit cell was utilized for all of the metal surfaces, and the p(2 × 1) unit cell was utilized for all of the metal oxide surfaces. The surface Brillouin zone was sampled by 3 × 3 × 1 **k**-points for all of the unit cells. The vacuum region between slabs was ∼10 Å, and a cutoff energy of 350 eV was used. Our pervious work shows that the above settings are accurate enough to give rise to correct reactivity trends.[17,18]
(17) Liu, Z.-P.; Hu, P. *J. Am. Chem. Soc.* **2002**, *124*, 11568; *J. Am. Chem. Soc.* **2001**, *123*, 12596.
(18) Michaelides, A.; Hu, P. *J. Am. Chem. Soc.* **2001**, *123*, 4235.
(19) Todorova, M.; Li, W. X.; Ganduglia-Pirovano, M. V.; Stampfl, C.; Reuter, K.; Scheffler, M. *Phys. Rev. Lett.* **2002**, *89*, 096103.
(20) Stampfl, C.; Ganduglia-Pirovano, M. V.; Reuter, K.; Scheffler, M. *Surf. Sci.* **2002**, *500*, 368 and the references therein.

JA030392K