Why Must Oxygen Atoms Be Activated from Hollow Sites to Bridge Sites in Catalytic CO Oxidation?

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There is no doubt that oxidation involving oxygen is one of the most important catalytic reactions:[1−5] Oxygen is a very active species and participates in many catalytic reactions, such as CO oxidation, epoxidation and fuel reforming. Taking catalytic CO oxidation as an example, which is very important not only technologically (in car exhaust emission control, CO_2 lasers, and air purification) but also scientifically, the elementary steps of CO oxidation at low and medium pressures are believed to be as follows:[1] (i) O_2 molecules dissociate on a metal surface, resulting in O atom chemisorption; (ii) CO molecules adsorb on the metal surface and then react with the chemisorbed O atoms, forming CO_2 (the Langmuir−Hinshelwood mechanism); and (iii) the product, CO_2, desorbs from the metal surface. Recently, Zhang, Hu, and Alavi[6] have found theoretically that there are two crucial events in CO oxidation on a Ru surface. First, O atoms must be activated from hollow sites (usually the most stable site) to bridge sites, and second, CO molecules have to approach the activated O atoms from the correct direction and at an appropriate time. The reaction barrier is predominately determined by O-metal bond breaking.[6,7] Experimental evidence[8−10] also suggests that O activation is essential. Then fundamental questions are the following: Why must O atoms be activated from hollow sites to bridge sites for CO oxidation to occur? Is it likely to be true for other oxidation reactions in heterogeneous catalysis? Obviously, these issues are fundamental for understanding catalytic oxidation and may also be important to catalysis in general. In this paper, we show that the necessity of the O activation is also true for CO oxidation on Rh(111). We aim to answer the above questions.

We carried out Density Functional Theory calculations for CO oxidation on Rh(111). A generalized gradient approximation[11] was utilized in the calculations. The electronic wave functions were expanded in a plane wave basis set and the ionic cores were described with ultrasoft pseudopotentials.[12] The surface was modeled by a p(2 × 2) unit cell with a slab of three layers of Rh(111). The vacuum region between slabs was 10 Å. A cutoff energy of 300 eV and 2 × 2 × 1 **k**-point sampling within the surface Brillouin zone were used. Recent work shows[13−16] that this set-up provides sufficient accuracy. In all the calculations, the bottom two layers of Rh atoms were held fixed in their bulk positions, while the top layer of surface atoms was allowed to relax. Transition states (TS's) were searched with a constrained minimization technique.[6,7,16] The TS is identified when (i) the forces on the atoms vanish and (ii) the energy is a maximum along the reaction coordinate, but a minimum with respect to all remaining degrees of freedom.

Two TS's for CO oxidation on Rh(111) have been identified, which are shown in Figure 1a,b. The reaction barriers from these two TS's are very similar, being 0.99 and 1.13 eV for TS's (a) and (b), respectively. These two TS's are similar in nature to those determined on Pt(111)[7] and Ru(0001):[6] the O atom is on the bridge site with the CO on the off-top site. We have searched for TS's with the O atom on or near the hollow site, and no TS could be found for the Langmuir−Hinshelwood mechanism: the O atom on the hollow site is not reactive. It is essential that the O atom must be activated from the hollow to a bridge site to achieve a TS on transition metal surfaces.

Why then is the O atom inactive for CO oxidation on the hollow site? We believe that an answer to this fundamental question lies in the manner O bonds to metal surfaces. We have calculated two chemisorption systems of Rh(111)-p(2 × 2)-O with O atoms on fcc hollow sites (inactive) and bridge sites (active). A plot of local density of states (LDOS) projected onto an O atom for O atoms on hollow sites is shown in Figure 2a. By examining the individual quantum states of the system, we found that the first peak from the left-hand side contains almost exclusively O 2s character. The large intensity of this peak indicates a high localization of electrons around the O atom. The second peak consists of some mixing states between strong O 2p and Rh d orbitals. Because of large charge accumulation between O and Rh atoms in these states, they can be considered to be 2p(O)−d(Rh) bonding states. The high intensities at low energies (centered around −5.6 eV) and very low intensities from −4.0 eV to the Fermi energy indicate that all the O 2p orbitals are almost used up by forming strong bonding with the metal atoms of the hollow site. Considering the fact that the O 2s is nearly fully occupied and the result above, one would expect that the O atom on the hollow site should be more or less "saturated". In particular, the O $2p_x$ and $2p_y$ (the p orbitals parallel to the surface) are "saturated". Consequently, the O atom is reluctant to bond with another species in the $x-y$ plane when it is on the hollow site. This is consistent with chemical intuition: The valence electron configuration of an O atom is

$$2s\ \underline{\uparrow\downarrow},\ 2p\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$$

and it will be more or less saturated when it bonds with three metal atoms on the hollow site. On the other hand, once the O moves to a bridge site, the O p orbital labeled as p_y, shown in the inset in Figure 3, does not mix strongly with metal d states. This can be seen clearly in Figure 3 in which special LDOS for O on the hollow and the bridge sites are illustrated. These LDOS are calculated by cutting a small volume (0.1 Å radius) around a point 0.4 Å away from the O atom center, which is the distance between the O atom center and the charge density maximum of p orbitals, along the p_x and p_y axis, respectively (the O 2s peaks for O on the hollow and the bridge site are similar and not shown). Figure 3 shows clearly that when O is on the hollow site the high charge densities are accumulated on those states with low energy levels on both p_x and p_y, and the charge densities between −4 eV and the Fermi level are relatively small, indicating the saturation of the O $2p_x$ and $2p_y$. In the case of O on the bridge site, however, there are obvious differences between p_x and p_y orbitals (the dotted lines in Figure 3a,b). In the LDOS cutting along the p_x axis, the

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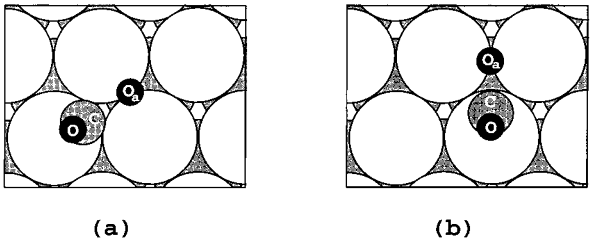

Figure 1. Two transition states for CO oxidation on Rh(111). The main structural features for these two TSs are summarized as follows. TS(a): Bond length $d_{\mathrm{C-O_a}} = 1.82$ Å, $d_{\mathrm{C-O}} = 1.17$ Å, $d_{\mathrm{C-Rh}} = 1.96$ Å; bond angle $\angle \mathrm{O_a-C-O} = 111.4°$. TS(b): Bond length $d_{\mathrm{C-O_a}} = 1.88$ Å, $d_{\mathrm{C-O}} = 1.17$ Å, $d_{\mathrm{C-Rh}} = 1.95$ Å; bond angle $\angle \mathrm{O_a-C-O} = 111.9°$.

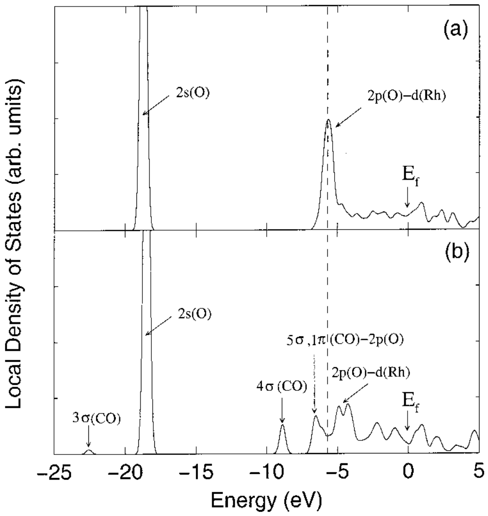

Figure 2. LDOS projected onto the chemisorbed O from (a) O chemisorption on the hollow site of Rh(111) and (b) the TS(a) for the CO oxidation reaction. The Fermi level is at zero. (a) The first peak: localized O 2s orbitals; the second peak: O 2p–Rh d bonding states. (b) The first peak and the third peak are due to the delocalization of the CO 3σ and the 4σ electrons into the O. The fourth peak contains mixing states between CO 5σ–O 2p and CO 1π–O 2p orbitals. After dashed line, the mixing states of O 2p–Rh d were mainly found.

difference between the O on the hollow and the bridge site is small, whereas along the p_y axis, the charge densities at the low energy levels for the O on the bridge site decrease considerably and more charge densities appear at high energy levels (the dotted line in Figure 3b). By examining individual quantum states, we found that in the p_y direction, the p-metal bonding is much weaker than that in the p_x direction and also there are some p–d antibonding states with significant densities near the Fermi level. Therefore, some O $2p_y$ orbitals are available to form new bonding and the O atom is reactive on the bridge site in this direction.

Naturally, the above argument can be used to explain why no TS is found for the O atom on or near the hollow site. To form a TS in CO oxidation, the O atom must bond, to some extent, with the CO. Because of the strong bonding of the O $2p_x$ and $2p_y$ with the three metal atoms of the hollow site (the second peak in Figure 2a), there are not enough O 2p orbitals available in the surface plane to bond with the CO. For a reaction to occur, therefore, the O atom must be activated from the hollow site to a lower coordination site (bridge site) to make some of its orbitals available. In other words, there is a substantial bonding competition between the CO and the metal atoms with the hollow site O atom. Once some bonding between the CO and the O atom is formed, the O–metal bonding would be weakened. Indeed this is what we have observed in the TS searches: When the CO is close enough to the O atom, the O atom moves away from the hollow site due to the weakening of the O–metal bonding. This can also be seen in the electronic structures of the TS's. A plot of local density of states projected onto an O atom from the TS(a) of CO/O/Rh(111) is shown in Figure 2b. After examining the quantum states in the TS, we found that the first and the third small peaks from the left-hand side are the consequences of the delocalization of the CO 3σ and the CO 4σ orbitals into the O atom, respectively. The second peak represents the localized O 2s orbital. The fourth peak, which is the most important to the present discussion, contains strong bonding states between CO 5σ–O $2p_y$ and also some CO 1π–O $2p_y$ orbitals. It is clear that they are formed at the expense of the ($2p_x$, $2p_y$)–d bonding: The peak intensity of the 2p–d bonding is much smaller in the TS (Figure 2b)) than that of the O atom on the hollow site (Figure 2a).

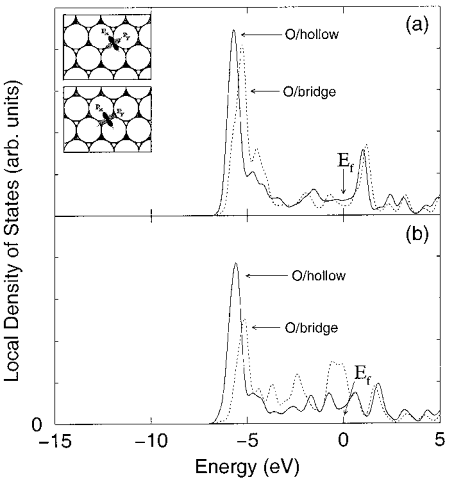

Figure 3. LDOS projected onto a small volume (0.1 Å radius) around a point 0.4 Å away from the O atom center along the p_x and p_y axis, respectively, for the O on the hollow and the bridge site. (a) LDOS along the p_x axis; (b) LDOS along the p_y axis. The inset depicts the bonding of O $2p_x$ and $2P_y$ orbitals with metal atoms. For the O chemisorption on the hollow site, both O 2p orbitals bond strongly with metal d states. For the O on the bridge site, one of the O 2p orbitals (grey) mixes much less strongly with metal d states than that of the other (dark). The metal d orbitals are not shown for clarity.

In summary, this is, to the best of our knowledge, the first attempt to explain why an O atom must be activated in CO oxidation on transition metal surfaces. Because of the saturation of O 2p orbitals in the 3-fold hollow site, the O atom is inactive. Thus it must be activated to a bridge site to form a TS. We predict that the activation of oxygen is likely to be a key event for other oxidation reactions. It should be stressed that although the conclusion may look simple, it is an important step toward an understanding of catalytic CO oxidation. Recently, some TS's for several catalytic reactions such as $CH_2 + H$,[17] $NH + H$,[17] $C + O$,[17,18] and $N + O$[17,19] were identified. It was found that the TS structures are similar to that in the CO oxidation we described above. We expect that our explanation discussed above may well be used to understand these reactions. Perhaps the most important result in this study is that we show that the chemistry of CO oxidation is determined by the O 2p orbitals. We expect that p orbitals also play an important role in determining the reactivities and reaction pathways of other molecules and fragments.

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