CO Oxidation on Pt(111): An *Ab Initio* Density Functional Theory Study

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(Received 11 December 1997)

CO oxidation on Pt(111) is studied with *ab initio* density functional theory. The low energy pathway and transition state for the reaction are identified. The key event is the breaking of an O-metal bond prior to the formation of a chemisorbed CO_2 molecule. The pathway can be rationalized in terms of competition of the O and C atoms for bonding with the underlying surface, and the predominant energetic barrier is the strength of the O-metal bond. [S0031-9007(98)05879-7]

It has been known for a long time [1] that the oxidation of CO can be effectively catalyzed by certain transition metals. This phenomenon has since come to prominence both for its intrinsic scientific interest and for its immense technological importance [2]. For example, car exhaust catalytic converters, widely used since the 1970's to remove CO and other pollutants from exhaust emission, have as their active components transition metals such as Pt, Pd, or Rh supported on metal oxides. Spurred by such technological interest CO oxidation on transition metal surfaces has become one of the most widely studied catalytic reactions [2–5]. It remains, however, inadequately understood. In order to provide insight into the development of new catalysts, two important questions can be phrased as follows: (1) What is the transition state in this reaction? (2) What is the physical origin of the reaction barrier? Answers to the second question are crucial since the reaction rate, i.e., the efficiency of the catalyst, decreases exponentially with the energetic barrier, and it is obvious that the answer to the first question must be sought before the second can be tackled. In this Letter we focus on these two issues.

We used a finite temperature formulation of density functional theory [6], using nonlocal pseudopotentials and a plane wave basis set, as implemented in the code FEMD [7]. In this method, the self-consistent electronic density is computed using an efficient iterative diagonalization [8] of a high-temperature density matrix, together with a conventional density-mixing scheme. Calculations were done using both the local density approximation (LDA) [9] and with gradient corrections (GGA) [10,11] to the LDA. We focused on a system that is well characterized experimentally: the $CO/p(2 \times 2)$-O/Pt(111) coadsorption system [12], in which the O atoms are chemisorbed on hollow sites in a $p(2 \times 2)$ structure, and CO adsorbed on top sites (Fig. 1). Our periodic system consisted of three layers of Pt atoms (four atoms per layer), two O atoms, and one C atom. In all the calculations, the bottom two layers of Pt atoms were held fixed in their equilibrium positions, while the top layer of atoms was allowed to relax. Soft pseudopotentials generated by using a kinetic-

energy-filter optimization scheme were employed, and the electronic orbitals were expanded up to 500 eV cutoff [13]. The pseudopotentials accurately reproduced the properties of the isolated systems, including equilibrium lattice constant of Pt, the CO bond length and vibrational frequency, and the CO_2 bond lengths and vibrational frequencies. Calculations were done using a Monkhorst-Pack mesh of $2 \times 2 \times 1$ and convergence with respect to k-point sampling was checked using a $6 \times 6 \times 1$ mesh. A realistic electronic temperature (800 K) in the finite temperature density functional was employed. We searched for the low energy pathway taking us from $CO/p(2 \times 2)$-O/Pt(111) to chemisorbed CO_2 using a constrained minimization scheme. In this approach, we keep the C-O(a) distance fixed at preselected values, and minimize the total energy with respect to all remaining orthogonal degrees of freedom. In particular this means that the molecules are free to rotate and translate subject to the above constraint, and in addition the surface Pt atoms are allowed to relax. The transition state (TS) is identified by requiring (a) that the ionic forces at the TS vanish and (b) that the TS is a maximum along the reaction coordinate [i.e., C-O(a) distance], but a minimum with respect to all remaining degrees of freedom. The resulting pathway gave a smooth passage from the initial to final state, which is shown in a series of snapshots in Fig. 2.
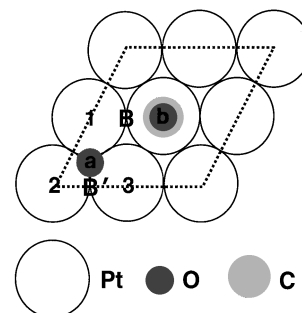

FIG. 1. The geometry of the $CO/p(2 \times 2)$-O/Pt(111) configuration. The unit cell in the surface plane is indicated with dotted lines.
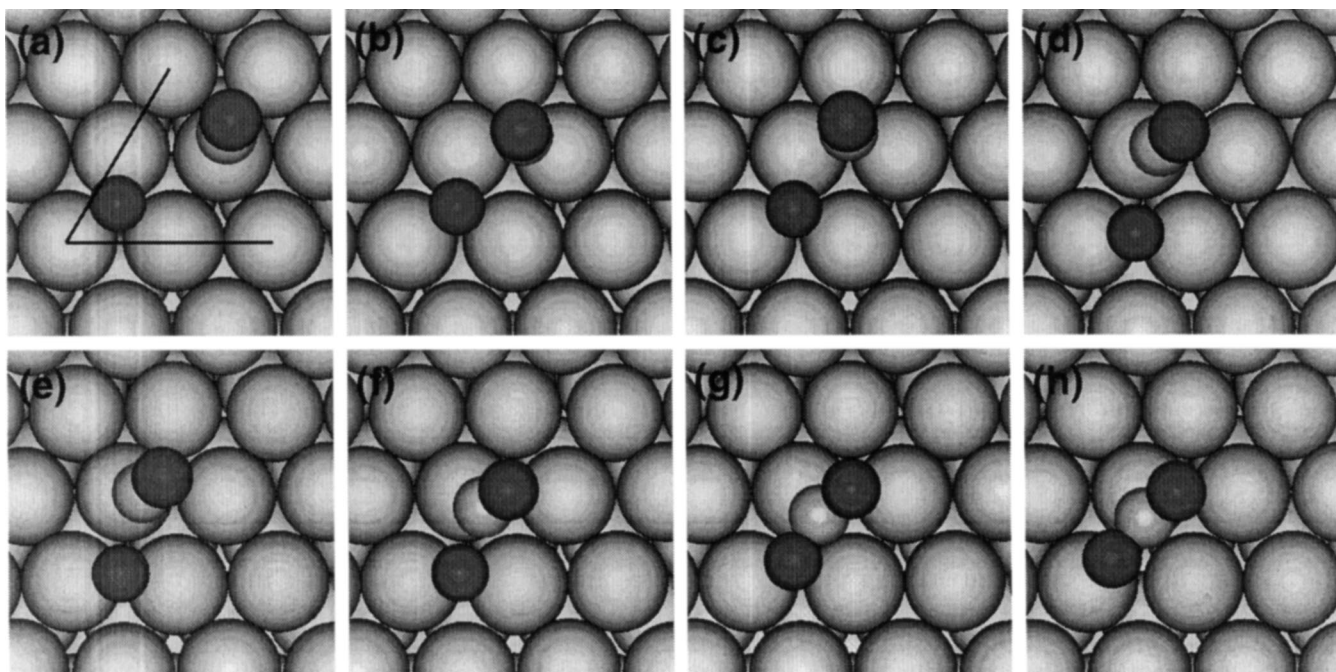
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FIG. 2. Snapshots of the reaction pathway from the initial state [top left, (a)] to the final state [bottom right, (h)]. The lattice vectors are indicated in (a). For clarity, the periodic images of the molecules are not shown, and the view is slightly tilted from the vertical. The Pt atoms are the largest spheres, the O atoms are the darkest spheres, and the small grey spheres are the C atoms. The transition state is (e). In (h), the molecular geometry of the CO_2 molecule is bond lengths C-O(a) = 1.29 Å and C-O(b) = 1.21 Å and bond angle 131°. The gas-phase molecule is linear with a bond length of 1.16 Å.

The initial motion in the reaction path is due to the CO molecule moving towards the bridge site B. As the CO molecule arrives at B, the O(a) atom is displaced a small amount away towards the opposite bridge site B' [Fig. 2(c)]. The next event is pivotal. The CO molecule moves from B onto Pt(1); the *O(a) atom simultaneously breaks its bond with Pt(1) and moves to B'* [Fig. 2(e)]. This is the transition state. In the next few steps the CO molecule and O(a) atom move together to form a bond, in the process of which a second O(a)-Pt bond [Pt(3)] is broken. This process is complete in Fig. 2(g). The nascent CO_2 thus formed, however, is in an unfavorable location on the surface and displaces itself to give finally chemisorbed CO_2, which is a highly bent and stretched molecule asymmetrically bonded with the surface [Fig. 2(h)], with O(a) bonded to Pt(2) and the C atom to Pt(1).

The chemical bonding changes dramatically in the course of this pathway. This can be seen by considering the changes in the electron density, which are displayed in two different ways in Figs. 3 and 4. Figure 3 shows the electron density in planes parallel to the surface. The motion of the CO molecule from the initial configuration to B results in the spreading of electron density to the neighboring Pt(1) atom, while breaking the threefold symmetry of the electron density surrounding O(a). In fact, the value of the minimum charge density ρ_{min} along the O(a)-Pt(1) axis precipitously drops from 0.12 to 0.08 a.u., *indicating that the presence of the CO molecule at B severely weakens that bond.* At the transition state,

the O(a)-Pt(1) bond is completely broken, and electron density contours indicate O(a) is bonded only to Pt(2) and Pt(3), while the CO molecule has become bonded to Pt(1). The formation of the nascent C-O(a) bond occurs at the transition state, where ρ_{min} has a small value 0.06 a.u., but which rapidly grows to 0.35 a.u. as the two species come together. The calculated reaction barrier is 1.01 eV in the LDA and 1.05 eV in the GGA [Fig. 3(c)]. Both are in good agreement with the barrier of approximately 1 eV deduced from kinetic experiments [3]. We remark that the difference in the energy barrier predicted by the LDA and GGA is found to be very small in the present system. The transition state has a very interesting feature: Distance between C and O(a) is remarkably long, 2.1 Å, compared to the bond length (1.16 Å) between C and O in CO_2 molecules. It indicates that the direct repulsion between chemisorbed CO and chemisorbed O atom may not be so important in generating the reaction barrier. To find the physical origin of the reaction barrier, we calculated O chemisorption energies on Pt(111) without CO. We found that O atoms bonded with three Pt atoms on hollow sites (the same as that in the initial state) are approximately 0.6 eV more stable than the structure with O atoms on bridge sites. Furthermore, the barrier to CO diffusion from a top site to a bridge site in the absence of chemisorbed O atoms is very small, whereas it is approximately 0.5 eV in the presence of such O atoms. The reason for this marked increase in energy is the weakening of the O-Pt(1) bond which occurs when the
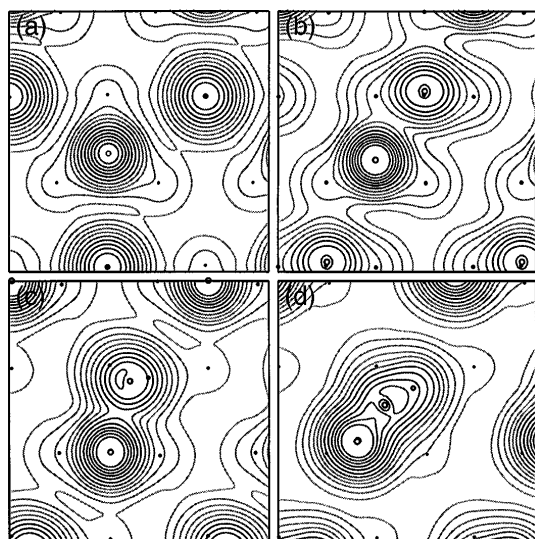
FIG. 3. Electron density contours parallel to the surface. The plane of the contours is chosen as midway between the z components of the C atom and O(a). The contours are logarithmically spaced. Black contours denote the highest electron density (H). The logarithmic spacing (S) is given below. Densities are in atomic units (a.u.). (a) $CO/p(2 \times 2)$-O/Pt(111) (H: 0.89, S: 0.63); (b) CO on B (H: 0.86, S: 0.68); (c) Transition state (H: 0.89, S: 0.65); (d) CO_2/Pt(111) (H: 0.89, S: 0.63).

FIG. 4. (a) and (b): ρ_{min} for the O(a)-Pt and C-O(a) bonds, respectively, along the reaction pathway. $\rho_{min}(A, B)$ is the lowest value of the electron density along the axis from atom A to atom B. The change in ρ_{min} is a convenient measure of the change in the strength of the chemical bond between A and B. The reaction coordinate is taken as the C-O(a) distance. (c) The energies of the eight configurations shown in Fig. 2, relative to the lowest energy configuration. Dashed line: LDA; solid line: GGA.

CO molecule is on the bridge site. The competition for forming surface bonds, therefore, results in a significant indirect repulsion between the CO molecule and the O atom, which generates a long transition state. The key role of the weakening and breaking of an O-Pt bond suggests that the predominant barrier to the reaction is the strength of this bond. Therefore, the barrier should be lower if the O-metal bonds are weakened. A similar feature has been discussed in CO oxidation on Ru [4].

These findings can explain many of the features found experimentally. The chemisorbed CO_2 species is a highly bent and asymmetric structure, with bond lengths substantially longer than in the gas-phase molecule. On desorption from the surface the molecule will be in highly excited vibrational states, as is observed experimentally [14]. Modification of the O atom environment, for example, by their adsorption at sites of surface defects or in disordered configurations, may weaken their surface bonds, and should therefore require lower energies for the reaction to proceed. Indeed this is observed experimentally [12], where the CO oxidation reaction occurs at lower temperatures when disorder is introduced in the O atom chemisorption. The paradoxical behavior of CO oxidation on Cu can similarly be explained. In this case, the reaction does not occur easily if the O atoms are chemisorbed at room temperature but takes place readily if they are chemisorbed at lower temperatures [15]. We suggest the reason for this behavior is that at room temperatures the chemisorbed O atoms are tightly bonded, be-
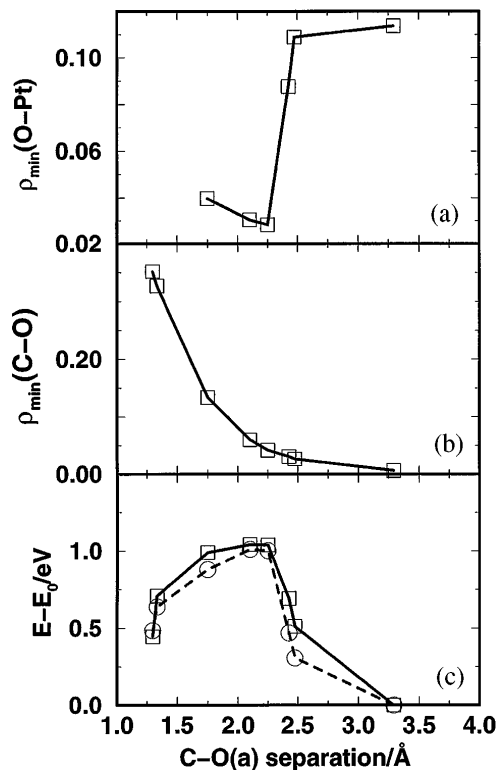
ing incorporated as Cu-O-Cu chains [16]. The energetic barrier to breaking such Cu-O bonds is highly unfavorable. On the other hand, O atoms chemisorbed at lower temperatures are more weakly bonded to hollow sites of the surface, and in this case the energetic barrier breaking a Cu-O bond is much lower, enabling the CO oxidation reaction to occur at low temperatures.

The observed pathway has the feature of least bond breaking. The initial motion of CO towards the bridge site B does not significantly weaken any chemical bond. At the transition state only one O-Pt bond is broken, and the competition for bonding is limited to only one Pt atom. In alternative pathways, for example, the linear trajectory taking the CO molecule to the O atom through a hollow site involves the competition for bonding of the CO molecule with two Pt atoms which are simultaneously bonded to the O atom. This weakens two O-Pt bonds and we explicitly verified that it is much more energetic (in excess of 2 eV). It is plausible and in keeping with general physical principles [17] that minimizing the competition for bonding with surface atoms and the number of broken surface bonds are general features

of reaction pathways in such systems. Such a simple geometric criterion may be a useful guide in identifying possible low energy pathways.

In this Letter we have identified a transition state and low energy pathway for CO oxidation on Pt(111) in the Langmuir-Hinshelwood mechanism for the first time, and provide microscopic evidence that the predominant barrier for the reaction is the strength of the bond between the O atoms and the surface. We expect that modifications of this may play a crucial role in determining the efficiency of the catalyst.

Note added.—After the submission of this Letter, an experimental (scanning tunneling microscopy) study of CO oxidation on Pt(111) was published [18], in which it was found that CO oxidation takes place more readily at the boundaries between O islands and CO islands. This finding is consistent with the results presented here since we expect that the O atoms at such boundaries may be displaced from their ideal $p(2 \times 2)$ sites and therefore provide a lower barrier to reaction with CO than interior oxygens.

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