Anomalous Behavior of Ru for Catalytic Oxidation: A Theoretical Study of the Catalytic Reaction $CO + \frac{1}{2} O_2 \rightarrow CO_2$

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Recent experiments revealed an anomalous dependence of carbon monoxide oxidation at Ru(0001) on oxygen pressure and a particularly high reaction rate. Below we report density functional theory calculations of the energetics and reaction pathways of the speculated mechanism. We will show that the exceptionally high rate is actuated by a weakly but nevertheless well bound (1×1)-oxygen adsorbate layer. Furthermore, it is found that reactions via scattering of *gas-phase* CO at the oxygen covered surface may play an important role. Our analysis reveals, however, that reactions via *adsorbed* CO molecules (the so-called Langmuir-Hinshelwood mechanism) dominate.   [S0031-9007(97)02370-3]

The oxidation of carbon monoxide at transition metal surfaces is one of the most extensively studied heterogeneous catalytic reactions (see, for example, [1–3], and references therein). Numerous investigations performed under ultra high vacuum (UHV) conditions for many different metal surfaces have shown that the reaction proceeds via the so-called Langmuir-Hinshelwood (L-H) mechanism, which means that the reaction takes place between *chemisorbed* reagents. Typical conditions for working catalysts, however, are higher pressure and temperature. Although it has been demonstrated that for a number of systems extrapolation of data over a wide pressure range is valid [4], such a conclusion cannot be generalized. Recent high gas pressure studies (e.g., at about 10 torr), for oxidizing conditions (i.e., at CO/O_2 pressure ratios <1) [3,5,6] reported that CO_2 production over Ru(0001) is anomalous: (1) The rate of CO_2 production was found to be exceptionally high—significantly higher than at any other transition metal surface. Interestingly, under UHV Ru(0001) is by far the poorest catalyst [1]. (2) The measured kinetic data (activation energy and pressure dependencies) were found to be markedly different to those for other substrates, and in contrast to the other transition metal catalysts, Pt, Pd, Ir, and Rh, highest rates occurred for high concentrations of oxygen at the surface. (3) Almost no chemisorbed CO was detected during or after the reaction. It was therefore speculated that the Eley-Rideal (E-R) mechanism is operational as opposed to the "usual" L-H mechanism [6]. In the E-R mechanism, the reaction occurs between *gas-phase* and chemisorbed particles. So far E-R mechanisms have been observed only experimentally for somewhat artificial reactions triggered by a beam of atomic hydrogen (or deuterium) [7]. To gain understanding into the drastically different behavior of Ru(0001) for the CO oxidation reaction, we carried out density functional theory (DFT) calculations, where the main approximations are the supercell approach and the employed functional for the exchange-correlation interaction. For the latter we use the generalized gradient

approximation (GGA) [8] which is the best justified treatment to date. Our study represents the first theoretical attempt to follow a heterogenous catalytic reaction [molecular and dissociative (atomic) adsorption, surface reaction, desorption of products] using DFT-GGA and an extended surface. In brief, the details of the theoretical approach are summarized as follows: We use *ab initio,* fully separable, norm-conserving DFT-GGA pseudopotentials [9]. The GGA is thus treated in a consistent way, from the free atom to the solid surface and the reactants. Relativistic effects are taken into account by using spin averaged potentials. The surface calculations are performed using a (2×2) surface unit cell, a four atomic layer Ru slab, and a vacuum region corresponding to thirteen such layers. We use an energy cutoff of 40 Ry with three special **k** points [10] in the two-dimensional Brillouin zone. Convergence tests for O on Ru(0001) indicated that this basis set provides a sufficiently accurate description [11]. The adsorbate structures are created on one side of the slab [12] where we relax the position of all the atoms using a damped molecular dynamics [13], except for the Ru atoms in the bottom two layers, which are kept at their bulklike positions. Details of the calculations will be published elsewhere [14].

It is well know that under UHV conditions, at room temperature, dissociative adsorption of O_2 results in a saturation coverage of $\Theta_O \approx 1/2$ corresponding to the formation of a (2×1) structure [15]. Recently, from DFT-GGA calculations we predicted that an even higher coverage should be stable on the surface, namely, a (1×1) structure with coverage $\Theta_O = 1$, where the O atoms occupy hcp-hollow sites [11]. Subsequently, this structure was indeed successfully created under UHV conditions [16], where it was concluded that formation of the $\Theta_O = 1$ structure from gas-phase O_2 is hindered kinetically [11,16], but by offering atomic oxygen (or under high pressure conditions), this phase can be attained. We also carried out calculations involving higher oxygen coverages on the surface, as well as geometries involving

subsurface oxygen; these structures were found to be unstable and metastable, respectively, with respect to gas-phase O_2. We therefore do not expect them to play an important role for the present investigation. We refer to Refs. [16,17] for more details. Because the conditions under which the particularly high rates of CO_2 formation occur involve elevated partial gas pressures (and CO/O_2 ratios <1), there will be a significant attempt frequency to overcome activation barriers for dissociative adsorption of O_2. Thus it is likely that during reaction the oxygen coverage on the surface approaches one monolayer. We therefore initially assume in our investigation of the oxidation of CO at Ru(0001) that the (1×1) phase covers the surface.

As mentioned above, from the experiments it had been speculated that CO may react from the gas phase with adsorbed oxygen (the E-R mechanism) [6]. To investigate this possibility we first ask whether CO can adsorb on the (1×1)-O/Ru(0001) surface. The sites considered were the on-top and fcc-hollow sites, with respect to the Ru(0001) substrate, and a bridge site between two adsorbed O atoms (compare inset of Fig. 1). For each site we calculated the energy as a function of distance of the molecule from the surface. In these calculations the CO axis is held perpendicular to the surface with the C end of the molecule closest to the surface. At each point we fix the position of the C atom and relax the positions of all the O atoms and the top two Ru layers. The results are shown in the left panel of Fig. 1, where we have also considered the path for CO directly above an adsorbed O atom. It can be seen that CO experiences an energy barrier which starts to build up at about 2.5 Å from the surface for all sites, reflecting a *repulsive* interaction with the O-covered surface. Furthermore, it is apparent that the surface potential is significantly corrugated: Considering a constant-total-energy surface as a function of the lateral position of the CO, we find that it exhibits the lowest energy (but always repulsive) over the fcc-hollow site. Thus CO tends to avoid the O adatoms but will not form a chemical bond with the metal substrate. The
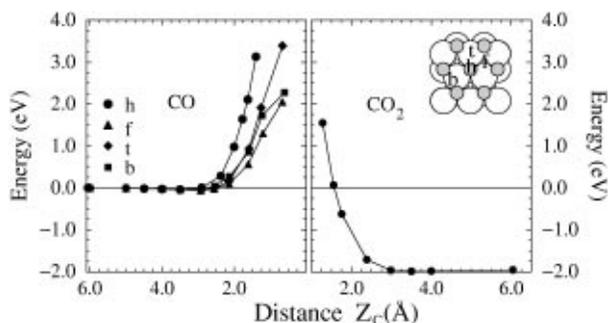

FIG. 1. Energy as a function of distance of the C atom, Z_C, of the CO and CO_2 molecules from the surface for the various sites tested. The molecular axes are constrained to be perpendicular to the surface. The zero of energy refers to the situation where CO is far away from the (1×1)-O/Ru(0001) surface ($Z_C \approx 6$ Å).

O-covered surface thus *prevents* reaction via the L-H process leaving the possibility for reaction via *gas-phase* CO with chemisorbed O, i.e., the E-R reaction. In this respect, for the approach of CO directly above an adsorbed O atom (full circles in Fig. 1), we find the initial, repulsive interaction turns into an attractive one, and the CO molecule and the adsorbed oxygen atom react to form CO_2. That is, the O-Ru adsorption bond switches over to form the CO_2 complex. (This is discussed in more detail below.) On relaxing the position of the C atom, the CO_2 molecule then leaves the surface with a significant energy gain of ≈ 1.95 eV. The associated energetics are shown in the right panel of Fig. 1. It is important here to emphasize that we have considered all relevant reaction paths for CO at the (1×1)-O/Ru(0001) surface and that although on first consideration Fig. 1 may appear to suggest that the favored reaction pathway for CO_2 formation is over sites away from the adsorbed O atom, in particular the fcc-hollow site, this is not the case: Indeed "slow moving" CO molecules with low translational energy will be "steered" towards the fcc-hollow sites. These molecules will, however, not achieve reaction due to the sizable energy barrier. Fast CO molecules of high translational energy, not susceptible to steering effects, which are incident at sites away from an adsorbed O atom will also not react, but will rather be reflected from the surface. Thus to produce CO_2 via this mechanism, the results indicate that the molecule must "hit," or get very close to, an adsorbed O atom. Interestingly, the calculations show that there is a physisorption well for CO, as well as for CO_2, above the surface (barely visible in Fig. 1). The wells are very shallow (≈ 0.04 eV) and thus they will not play a role. It should be noted, however, that the calculated depths are likely to be lower bounds because the employed exchange-correlation functional does not describe the long-range (van der Waals type) interactions and the physisorption wells are found at distances where the true potential energy is likely to be more attractive than that given by the DFT-GGA calculation.

A more detailed understanding of the pathway for reaction via scattering of CO is obtained by evaluating an appropriate cut through the high-dimensional potential energy surface (PES); thus cut is defined by two variables: the vertical position of the C atom and the vertical position of the O adatom below the molecule. In order of ease of analysis, the CO axis is initially held perpendicular to the surface. The resulting PES is presented in Fig. 2, where the coordinate system is shown as the inset. For each point we relaxed all the O atoms (except that held fixed at Z_O), and the top two Ru layers. The repulsive interaction is again evident as CO nears the surface. In response to the approaching molecule, the O adatom moves in towards the surface: For example, at a distance of $Z_C = 1.9$ Å, the O atom is displaced inwards by $Z_O = 0.2$ Å. Thus the impinging CO molecule "hits" a "soft wall." Reaction to CO_2 is achieved via an upward
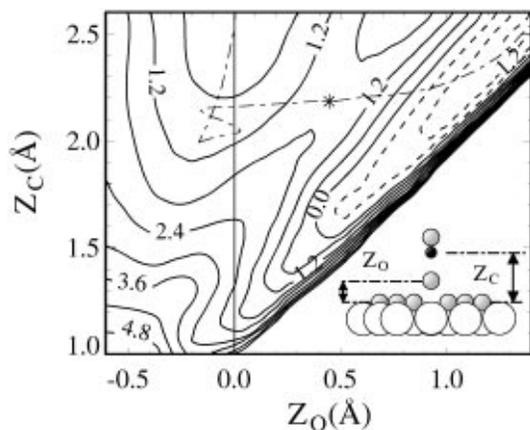
FIG. 2.   Cut through the high-dimensional potential energy surface (PES) as a function of the positions of the C atom, Z_C, and the O adatom, Z_O (see inset). The molecular axes are constrained to be perpendicular to the surface. Positive energies are shown as continuous lines, negative ones as dashed lines. The contour-line spacing is 0.6 eV. The dot-dashed line indicates a possible reaction pathway.
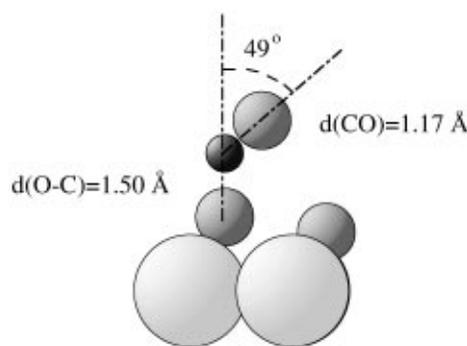

FIG. 3.   Transition state geometry identified for the reaction of gas-phase CO with adsorbed oxygen when the constraint on the molecular axis is relaxed. The large, medium, and small circles represent Ru, O, and C atoms, respectively.

movement or "hop" of the O adatom by ≈ 0.4 Å towards the CO molecule (corresponding to movement parallel to the horizontal axis of Fig. 2) and brings the system to the transition state of the reaction marked by the asterisk. In view of the similar masses of O and C, it is likely that the impinging CO molecule will impart a significant amount of energy to the O adatom, thus stimulating its vibrations and facilitating its motion (indicated by the oscillations in the dot-dashed curve). The newly formed CO_2 molecule then finds itself in a particularly unfavorable position and is strongly repelled from the surface towards the vacuum region with a large energy gain of 1.95 eV. In the cut through the PES shown in Fig. 2, the energy barrier hindering CO_2 formation is ≈ 1.6 eV.

The PES of Fig. 2 corresponds to a constrained situation of the surface-CO angle. When this constraint is dropped, i.e., when the tilt angle of the CO axis is allowed to relax [18], we find that the energy barrier is reduced to 1.1 eV, and also that the position of the saddle point of the PES occurs closer to the surface (by 0.3 Å). At the transition state (see Fig. 3), the optimum tilt angle with respect to the surface normal is found to be 49°, which corresponds to a bond angle of 131° for the "CO_2-like" complex. Interestingly, this geometry is very similar to that associated with the CO_2^- ion [19] and to that proposed for the "activated complex" for the CO oxidation reaction over other transition metal surfaces [20].

We have thus identified a likely reaction pathway for the E-R mechanism. The activation energy barrier for this type of reaction appears to be sizable. However, it is very similar to those derived from experimental studies of CO oxidation reactions at other surfaces [3] which proceed via a L-H process, and also for the measurements at Ru(0001) the estimated activation energy is comparable, namely 0.85 eV [3,5,6]. On the basis of the present results we

predict an energy diagram for the E-R mechanism, which is shown in Fig. 4. An estimate of the reaction rate gives $R = 7.5 \times 10^6 \exp[-1.1/(k_B T)]$ s^{-1} which yields at $T = 500$ K, $R = 6 \times 10^{-5}$ CO_2 molecules formed per surface Ru atom per second [21] which is about 3×10^{-6} smaller than that observed experimentally [5]. This indicates that this mechanism alone cannot explain the particularly high CO_2 turnover rate. Nevertheless, the rate is only about a factor of 10^{-3} less than that for the L-H process at Pt or Pd [3] and with *molecular beam* experiments this predicted E-R mechanism and associated energetics could possibly be measured for the first time for the CO oxidation reaction.

To understand the high reaction rate reported experimentally, we turn to another consideration: CO molecules might adsorb at sites at which an oxygen atom has been removed (e.g., by the above described E-R reaction). Indeed, assuming thermal equilibrium of the CO + O_2 gas and a mixed CO + O adlayer, the law of mass action indicates that about 0.03% of the sites of the (1 × 1) adlayer will be occupied by CO (we assumed that the O_2 and CO partial pressures are equal, the temperature is $T = 500$ K, and the binding energy of CO into an O vacancy of the (1 × 1) adlayer is calculated to be 0.85 eV and the adsorption energy of $\frac{1}{2}O_2$ (i.e., an O atom) into a vacancy is 1.20 eV. In reality the CO concentration will
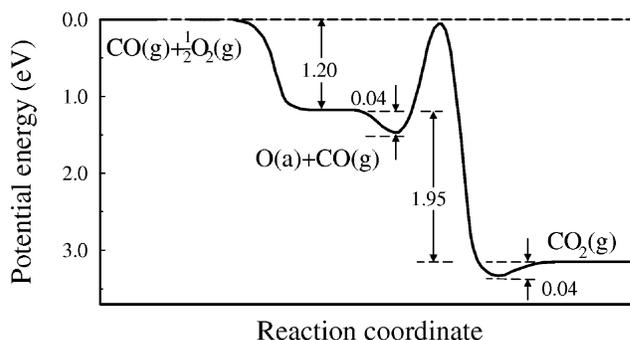

FIG. 4.   Calculated energy diagram for the E-R mechanism of CO oxidation at Ru(0001). Note that the depths of the physisorption wells are exaggerated for clarity.

be even higher because catalysis is not ruled by thermo-dynamic equilibrium but by kinetics, and we find that CO adsorption into an existing O vacancy can proceed basi-cally without hindrance while O adsorption (from O_2) is hindered by an energy barrier (see, e.g., Ref. [16]). There-fore the actual percentage of surface sites occupied by CO will be somewhat larger. For these CO molecules there is a substantial attempt frequency to form a CO_2 mole-cule with neighboring O adatoms, now by the L-H mecha-nism which we expect to proceed very efficiently due to the relatively weak binding energy of *both* CO (which we calculate to be about half that which it has on the clean surface—and on the surface with O coverages: $\Theta \leq 0.5$) and O atoms in the high-coverage (1×1) adlayer, as well as the close proximity of the constituents. We find that the energy gain on CO_2 formation (of the surface reaction) via this mechanism is about 0.66 eV [22]; noticeably smaller than that of 1.95 eV (see Fig. 4) but still quite significant if compared to that of ≈ 0.2 eV at Pt(111) and Pd(111) [1] as determined experimentally.

In summary, we now have the following picture of CO oxidation at Ru(0001): With respect to other transition metals, ruthenium binds oxygen particularly strongly. Therefore, at low oxygen coverages a Ru catalyst dis-sociates O_2 efficiently, but (in contrast to, e.g., Pd) it holds the oxygen (and CO) so strongly that reaction to CO_2 is disfavored. A good catalyst should actuate this dissociation but at the same time should not bind the dissociated entities too strongly, which gives them good capability to diffuse and react. Too strongly bound constituents would have little reason to react at all. For oxygen in the (1×1)-O monolayer, the adsorption energy is significantly weaker and thus CO_2 formation enhanced. Our results indicate that this high coverage oxygen phase enables reaction via both scattering of CO (the E-R mechanism) and by the L-H mechanism where the former may play an important role in initiating the reaction. The high rate then develops and is maintained by an efficient L-H mechanism. Our theoretical results thus explain the anomalous dependence of the reaction on oxygen pressure, as only under sufficiently high oxygen pressure the (1×1) layer is attained.

The different mechanisms identified in our study are also likely to play important roles for other catalytic reactions. We hope that the detailed predictions and the unusual mechanism outlined above will be tested by additional experiments.

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[21] For our estimate we use the frequency of impinging CO molecules per surface Ru atom of $\nu = 7.5 \times 10^6$ s^{-1} which corresponds to a CO gas phase pressure of 16 torr.

[22] This value is obtained as the reaction energy of CO + $\frac{1}{2}O_2 \rightarrow CO_2$ in vacuum, minus the energy gained on adsorption of $\frac{1}{2}O_2$ and CO onto the surface.