

Communications to the Editor

A General Mechanism for CO Oxidation on Close-Packed Transition Metal Surfaces

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CO oxidation on metal surfaces is one of the most important catalytic reactions due primarily to two reasons.^{1–3} Technologically, it is a very important reaction in car-exhaust emission control, CO₂ lasers, air purification, and sensors. Scientifically, it is one of the simplest catalytic reactions and thus is widely used as a model system to understand heterogeneous catalysis. Despite a large volume of work devoted to it, developments fall much short of chemists' expectations. In this paper, we investigate CO oxidation pathways on Ru(0001) using density functional theory (DFT) and generalize some common features for this catalytic reaction on transition metal surfaces.

It is believed, in general,^{1–5} that the CO oxidation follows the Langmuir–Hinshelwood mechanism. It is also well-known that Pt is one of the most active metals for CO oxidation, while Ru is one of the poorest at low pressures of O₂ and CO, being active only at high O₂ partial pressures, where the reaction mechanism is believed to be Eley–Rideal type.⁶ Very recently, a CO oxidation pathway on Pt(111) was identified.⁴ In this study, we investigate the pathway for CO oxidation on Ru(0001). We aim to answer the following questions: (i) What is the minimum energy pathway for the CO oxidation on Ru(0001) at medium coverage of oxygen? (ii) What are the common features in the CO oxidation mechanism on closed-packed active and inactive transition metal surfaces?

We performed DFT calculations using nonlocal pseudopotentials with a plane wave basis set.^{4,7} The surface was modeled by a p(2 × 2) unit cell with three layers of Ru(0001). Calculations were carried out using a generalized gradient approximation (GGA).⁸ In all the calculations, the bottom two layers of Ru atoms were held fixed in their bulk positions, while the top layer of atoms was allowed to relax⁹ (details of the calculations in ref 4).

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(9) Optimized normconserving pseudopotentials and 2 × 2 × 1 k-point sampling in the 2 × 2 surface Brillouin zone were used. Convergence checks for the cutoff energy (up to 650 eV), other GGA functionals (PBE) (Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865), a finer k-point sampling (4 × 4 × 1), and an increased number of slab layers (four) have been performed. It was found that the activation energy changed by less than 0.1 eV.

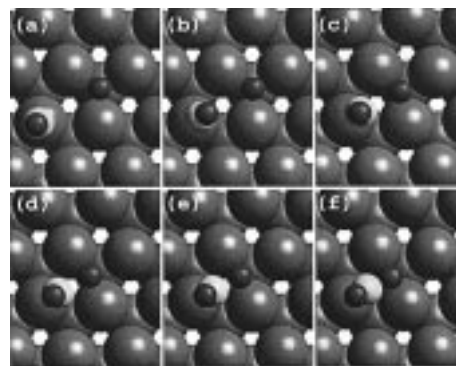


Figure 1. Snapshots of the reaction pathway from the initial state (a) to the final state (f).

Table 1. Comparison between the Calculated Structure and the Experimental Result for Ru(0001)–p(2 × 2)–(CO + O_a)^a

	calcd	exptl
bond length of CO, Å	1.147	1.16 ± 0.06
bond length C–Ru, Å	1.937	1.93 ± 0.06
bond length O _a –Ru, Å	2.049	2.06 ± 0.08
	2.049	2.06 ± 0.08
	2.052	2.09 ± 0.14
layer distance d ₁₂ , Å	2.111	2.09 ± 0.04
vertical buckling, Å	0.039	0.06 ± 0.04
tilt angle of CO, deg	4.5	12.6 ± 4.5
chemisorption energy of O, eV	5.67	
	5.55 ^b	
chemisorption energy of CO, eV	1.97	1.65 ^c

^a The experimental CO chemisorption energy is at Θ = 0.33 ML.

^b Reference 11. ^c Reference 12.

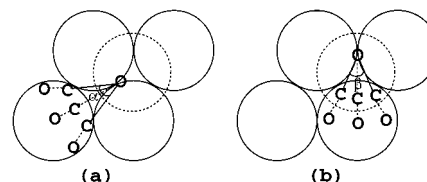


Figure 2. Two distinct transition-state geometries for the CO oxidation on Ru(0001). In the regions of α = 26° and β = 20° for (a) and (b), respectively, the energy difference is less than 0.01 eV.

The initial state of the CO oxidation (Figure 1a) is Ru(0001)–p(2 × 2)–(CO + O_a), where the O_a is an adsorbed O atom and is well characterized experimentally.¹⁰ Our calculated geometrical structure agrees with the experimental one very well (Table 1). After the reliable initial state of the reaction was obtained, more than 10 possible transition states (TSs) were searched, and it was found that there are two distinct TSs with low energies. TSs were verified by an eigenvalue analysis of their Hessian matrixes, which contained only one negative eigenvalue. It was also found that displacing the CO molecule in the vicinity of the TSs, keeping the C–O_a distance fixed, is a very soft mode, shown in Figure 2.

Once we obtained the TSs, the minimum energy pathway was located by combining the results of two ab initio molecular dynamics (MD) calculations, in which the TS(a) (Figure 2a, 0.1 eV lower than the TS(b)) was chosen as the starting point. In the first MD calculation,¹³ both the O_a and the C were given an initial

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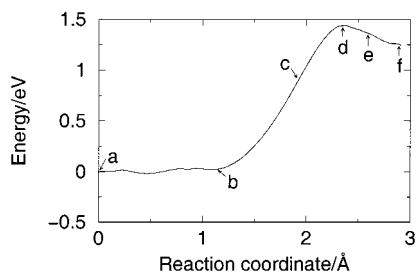


Figure 3. Energy change relative to the initial state as a function of the reaction coordinate. The reaction coordinate is defined as the total distance of the C and the O_a moved along the minimum energy pathway relative to the starting point in the reaction.

kinetic energy of 0.05 eV along the C– O_a bond direction, which pushes them together. The second MD calculation was the same as the first one, except that the velocity was in the opposite directions. As expected, the first MD gives rise to CO_2 formation, while the second MD leads to the initial state.

Several snapshots from the minimum pathway are shown in Figure 1. The energy change along the minimum energy pathway is shown in Figure 3. The pathway can be approximately divided into three steps: (i) The CO moves toward the O_a , while the O_a remains essentially on the hollow site (Figure 1b). (ii) The O_a moves from the hollow site toward the bridge site, while the C continues to move toward the O_a and the O atom above the C moves backward, leading to a completely different tilting angle (Figure 1c). The TS is reached when the distance between the C and the O_a is 1.73 Å (Figure 1d). (iii) After the TS, the CO continues to move toward the O_a , leading to the formation of a CO_2 . From Figure 3, the reaction barrier was determined to be 1.4 eV, which is consistent with the experimental estimation.¹²

Comparing CO oxidation on Ru(0001) and Pt(111),⁴ we find the following features. First, the transition states of the reaction are very similar in these two systems: the O_a is on a bridge site, while the CO is off a metal atom, tilting away from the O_a atom.

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(13) To obtain the minimum energy pathway, at each MD step the velocity was reset to zero, and the masses of Pt, C, and O were set to be the same.

Second, the reaction pathways of both systems possess some similarities: the first step is the CO movement, with little energy change, and the decisive step in the reaction is the O_a movement from a hollow site to a bridge site, with a substantial energy change. From these two systems, we build the following picture for CO oxidation at medium coverage. First, a CO molecule moves quite freely around its initial position, with little energy change, while an O_a vibrates in its three-fold hollow position. Separate MD calculations show that a considerable period of time can be spent in this local equilibrium. The O_a then becomes activated and moves to a bridge site. If the CO moves toward the O_a in the correct direction within an appropriate time (because the O_a on the bridge site is not stable, and thus the lifetime is very short), then the transition state can be achieved. These results and other preliminary results from Pd(111) suggest that two events are crucial in the CO oxidation: (i) the O_a atom has to be activated from a hollow site to a bridge site and (ii) CO has to approach the O_a atom in the correct direction (Figure 2) and at an appropriate time (when the O_a is on the bridge site). Obviously, these microscopic details are the basis for understanding catalytic CO oxidation and may provide insight into heterogeneous catalysis.

Although CO oxidation on both Pt(111) and Ru(0001) have crucial common features, the reaction barrier on Pt(111) was determined to be ~ 1.0 eV⁴, which is much lower than the barrier of 1.4 eV on Ru(0001). The lower activation energy on Pt(111) compared to Ru(0001) can be correlated with lower chemisorption energy of O_a and CO (4.21 and 1.67 eV, respectively, on Pt(111), and 5.67 and 1.97 eV, respectively, on Ru(0001)), implying weaker adsorbate and substrate bonding on Pt. To achieve the TS on Ru, therefore, the O_a and CO must approach each other closely, to weaken the O_a –metal and OC–metal bond. Indeed, this was to be the case: the C– O_a distance at the TS on Pt(111) is 2.10 Å, whereas it is significantly shorter (1.73 Å) on Ru(0001).

In summary, this work represents the first attempt to generalize important features of CO oxidation on close-packed transition metal surfaces in microscopic detail. The mechanistic details presented here will help us build a comprehensive picture of CO oxidation.

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