LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2001 issue.

NOTES

Mechanism for the high reactivity of CO oxidation on a ruthenium−oxide

Zhi-Pan Liu and P. Hu[a)]
School of Chemistry, The Queen's University of Belfast, Belfast, BT9 5AG, United Kingdom

Ali Alavi
Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom

Ruthenium is notably one of the poorest catalysts for CO oxidation under conditions of low and medium oxygen coverages, but turns out to be superior to Pt and Pd if operated in excess O_2. This puzzling anomaly, introduced by the so-called ''pressure gap,'' has been the subject of many studies,[1–8] both theoretically and experimentally. Three stages have been found for CO oxidation on Ru(0001) as the total O concentration increases.[5–8] (1) Under UHV conditions, dissociative adsorption of O_2 under low-pressure leads to apparent saturation at a coverage $\theta = 0.5$ monolayer (ML).[2] The CO/CO_2 conversion rate at this coverage is less than 6×10^{-5} for $T < 500$ K. Using density functional theory (DFT) calculations, Zhang, Hu, and Alavi have located the minimum energy pathway for CO oxidation on Ru(0001) at 1/4 ML coverage.[3] It was found that the reaction mechanism is very similar to that on other close-packed transition metals[4] but with a substantially higher barrier. (2) At O coverages above 0.5 ML, but lower than 3 ML, which is represented by (1×1)-O phase, the CO/CO_2 conversion rate is slightly higher than that at stage 1,[5] but is always below 2×10^{-4}. Theoretical work of Stampfl and Scheffler also shows a high reaction barrier at this stage.[6] (3) As the total O_2 coverage exceeds the equivalent of about 3 ML, the CO/CO_2 conversion probability increases significantly, being about 10^{-3} at low temperatures and jumping to about 10^{-2} when temperature exceeds 500 K.[5]

Although the debate concerning the reason for the enhanced activity of stage 3 still persists,[5–9] a recent paper[9] by Over *et al.* using LEED, STM, and DFT demonstrated that the active part of this ''O-rich'' phase is RuO_2, which grows epitaxially with its (110) plane parallel to the Ru(0001) surface. They found that CO adsorbs at a coordinately unsaturated Ru site (Ru_{cus}) and suggested that it reacts with a neighboring lattice oxygen to form CO_2. Despite this breakthrough, microscopic details of CO oxidation on RuO_2(110) are still missing. Aiming to shed light on CO oxidation on RuO_2(110), we have performed DFT calculations for CO oxidation on RuO_2(110). All the calculation details are described in Ref. 10.

CO chemisorption on RuO_2(110), namely, the initial state (IS) of CO oxidation, was first calculated.[11] The optimized geometrical, structure is shown in Fig. 1(a), in which the CO adsorbs on a top site of Ru_{cus} with a calculated chemisorption energy of 1.66 eV. Considering that on the RuO_2(110) surface only two different lattice oxygen atoms exist, O_{3f} and O_{br}, their bonding energies have been determined firstly to decide which O atom is mostly likely to be involved in CO_2 formation. We found the O_{3f} (7.40 eV) is much more strongly bonded than the O_{br} (5.64 eV), which is consistent with the experimental observation that the O_{br} row disappears after CO oxidation. Thus transition states (TS) were searched with constrained minimization technique.[3,12,13] The TS is identified when the O_{br}−CO distance reaches 1.71 Å, where (i) the force on the atoms vanish and (ii) the energy is a maximum along the reaction coordinate (the O_{br}−CO distance), but a minimum with respect to all remaining degrees of freedom. Previous work[6,12,13] shows that for this type of system, the relative error in the TS is considerably smaller than the barriers of concern in this paper.

The geometry of the TS is shown in Fig. 1(b). It can be seen that to reach the TS the displacement of CO is larger than that of O_{br}, and the C−Ru distance is remarkably lengthened (2.07 Å at the TS, 1.88 Å at the IS). The reaction barrier is calculated to be 1.15 eV. It should be stressed that this barrier is considerably lower than that on Ru(0001) [1.45 eV in $p(2 \times 2)$ cell], indicating a high reactivity of RuO_2(110) for CO oxidation.

To shed light on the high reactivity of RuO_2(110), we have calculated the local densities of states (LDOS) projected onto O_{br} atom at the IS and the TS, shown in Fig. 2. The LDOS is calculated by cutting small volumes with a 0.1 Å radius around 0.4 Å away from the O_{br} center in the y directions. This is the distance between the O_{br} atom center and the charge density maximum of the p_y orbital. It is seen that at the IS the larger portion of the p_y electrons, as in peak A (nonbonding $O 2p_y$), are located at high energies, compared to the LDOS from the O atom on metal surfaces.[4] Considering the ionic bonding nature in RuO_2,[14] it is these occupied high-energy states that make the O_{br} unusually re-
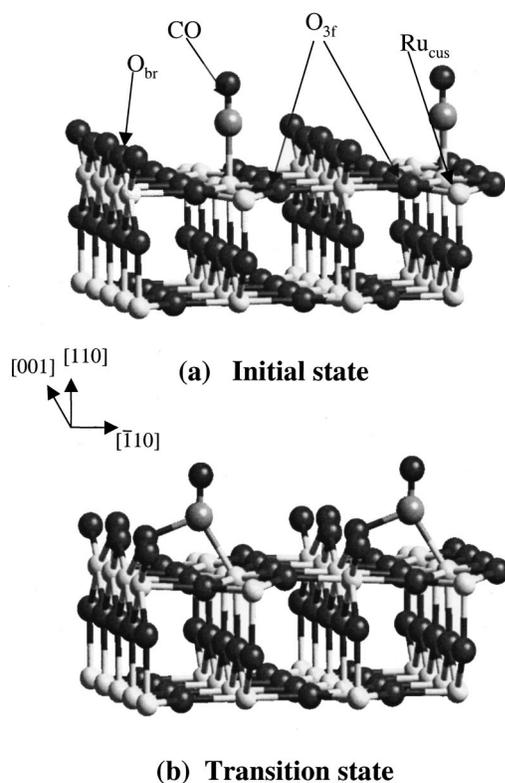
(a) Initial state

(b) Transition state

FIG. 1. (a) Ball and stick model for the bridging O terminated $RuO_2(110)$ surface on which CO adsorbs (the initial state of CO oxidation). (b) Ball and stick model for the transition state, in which CO bonds with a bridging O at a distance 1.71 Å. Only a part of calculated surface is shown. White, black, and gray balls represent the Ru, O, C atom, respectively. Coordinately unsaturated Ru atom (white atom, Ru_{cus}) as well as bridging O_{br} and threefold coordinated O_{3f} atoms are indicated by arrows.

active. Since the nonbonding electrons (peak A) can be readily donated to CO 2π orbitals, contributing substantially in O–CO bonding (peak B) formation without much energy loss in original O_{br}-surface bonding, the reaction barrier thus can be greatly reduced. In contrast, on Ru(0001) it has been found that the O_{ad}–CO bond formation leads to the great reduction of metal–O_{ad} and metal–CO bonding.[3,4] Therefore, the high activity of the O_{br} on $RuO_2(110)$ is not due to its bonding energy with the surface being low [in fact its bond strength is quite similar to that of adsorbed O_{ad} on the Ru(0001) surface[3]], but results from the bonding nature of O_{br} on the metal oxide surface.
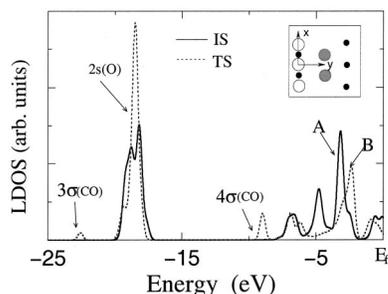
FIG. 2. LDOS projected onto a small volume (0.1 Å radius) around a point of 0.4 Å away from the O_{br} atom center along the y direction for the O_{br} at the IS (solid line) and the TS (dotted line). The insert in (a) depicts the x and y direction of O_{br} (big, white circle) in a top view of the $RuO_2(110)$ surface. Black (small) circle and gray (big) circle represent Ru_{cus} and O_{3f} atoms, respectively.

It is worth mentioning that we have also found the thickness of metal oxide film affecting the reactivity. A similar DFT calculation with 5 layers of $RuO_2(110)$ yields a reaction barrier of 0.80 eV. We expect that in real experiments, the reactivity of metal oxide may be affected by its thickness. To date, we have not found the reaction barriers reported from experiments for CO oxidation on $RuO_2(110)$, and thus a direct comparison between our calculated barriers and experimental ones is not available. However, considering the experimental observation that the CO oxidation is relatively slow below 400 K and reaches a plateau above 500 K,[5] the reaction barrier obtained from our calculations are reasonable.

In conclusion, this work represents one of the first attempts to study CO oxidation on a metal–oxide surface in microscopic detail. The TS and the reaction barrier on $RuO_2(110)$ are determined and the thickness of the $RuO_2(110)$ film was found affecting the reactivity. The electronic structure of the IS and the TS are analyzed, which should shed light on the high reactivity of $RuO_2(110)$ and the anomaly of Ru under high oxygen pressure.

a)Author to whom correspondence should be addressed. Electronic mail: p.hu@qub.ac.uk

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[10] A generalized gradient approximation [J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pedeson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992)], plane wave basis set for electronic wave functions and ultrasoft pseudopotentials [D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990)] were utilized in the calculations. It was found to be crucial to include explicitly the semicore electrons $(4s,4p)$ of Ru. The surface was modeled by nine layers of $RuO_2(110)$. The vacuum region between slabs was 9 Å. The unit cell utilized was (1×2), which was large enough to ensure no direct lateral interaction of adsorbed CO on the surface. A cutoff of 350 eV and $2\times2\times1$ **k**-point sampling within the surface Brillouin zone were used. In all the calculations the central five layers of $RuO_2(110)$ were held fixed while the other four layers were allowed to relax. 450 eV cutoff, $4\times4\times1$ **k**-point sampling and allowing partial occupations were used to further check our results.
[11] Tests for the lattice constants [calc.: 4.52×3.09 Å; expt.: 4.49×3.11 Å (Ref. 15)] of RuO_2 and the cohesive energies of both the Ru metal (calc.: 28.13 eV; expt.: 27.89 eV) and RuO_2 [calc.: 15.90 eV; expt.: 15.07 eV (Ref. 15)] were carried out and found to compare satisfactorily with experiments.
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