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Molecular origins of surface poisoning during CO oxidation over RuO₂(1 1 0)

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ABSTRACT

Metal oxides are of interest as environmental oxidation catalysts, but practical applications are often limited by poorly understood surface poisoning processes. RuO₂ is active for CO oxidation under UHV conditions but is deactivated by some surface poisoning processes at ambient pressures. In this work, we report kinetic models of surface poisoning during CO oxidation over RuO₂(1 1 0), based on data obtained from plane-wave, supercell DFT calculations. While a surface carbonate (CO₃²⁻) is stable at low O₂ pressures and high CO₂ exposures, it is not stable under catalytic conditions. A surface bicarbonate (HCO₃⁻) is more stable and deactivates the RuO₂ surface over a wide range of CO and oxygen pressures in the presence of trace amounts of water.

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1. Introduction

The deactivation of metal oxide catalysts by surface poisoning has long been recognized as an obstacle to their practical use [1,2]. The oxide anion is Lewis basic, making the metal oxides particularly susceptible to reaction with acidic gases, like NO_x, SO_x, and CO₂ [3,4]. For example, the highly active CO oxidation catalysts hopcalite (a mixture of manganese and copper oxides) and alumina-supported cobalt oxide are both susceptible to such deactivation in the presence of only trace amounts of moisture [5,6].

CO oxidation over RuO₂(1 1 0) has been studied extensively as a model for metal oxide catalysis [7–16]. RuO₂ is catalytically active for CO oxidation under ultrahigh vacuum (UHV) conditions [10]. Surface poisoning has been observed and attributed to the formation of an inactive surface carbonate, both on the basis of *ex situ* vibrational spectroscopy [17,18] and scanning tunneling microscopy [19] experiments. Deactivation at ambient O₂ pressures was also reported recently [20,21]. The exact nature of this surface poisoning and the mechanism of its formation are not clear. Whether the carbonate species observed *ex situ* is responsible for activity loss, as well as the precise nature of this carbonate species, remain to be resolved.

In this work we report kinetic models exploring the effect of carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) formation on CO oxidation rates over the RuO₂(1 1 0) surface, using data obtained from plane-wave, supercell DFT calculations [22]. We demonstrate that both carbonates and bicarbonates diminish the rate of CO oxida-

tion by surface site blocking and characterize the conditions under which such poisoning is expected to occur. The results are consistent with the high oxidation activities observed under UHV conditions and the diminished rates observed at ambient pressures. Bicarbonates are more stable than carbonates, are expected to form under conditions typical of CO oxidation, and likely account for the experimentally observed surface deactivation.

2. Computational details

Periodic supercell, plane-wave density functional theory (DFT) calculations were performed using version 4.6.26 of the Vienna ab Initio Simulation Package (VASP) [23]. Core-valence electron interactions are treated within the projector augmented wave (PAW) approximation [24,25]. Electronic energies and forces were calculated within the non-spin-polarized generalized gradient approximation (GGA) using the PW91 functional.

Most calculations are performed within a tetragonal 3 × 1 surface supercell, which includes three Ru_{cus} ions. A 6 × 8 × 1 Monkhorst–Pack mesh is used to sample the first Brillouin zone (12 symmetry-unique *k*-points). Plane waves are included to a cutoff energy of 400 eV. More computational details can be found in previous publications [22,26]. These parameters were sufficient to converge calculated energies to <0.01 eV and gradients to <0.03 eV/Å.

3. Results and discussion

The stoichiometric RuO₂(1 1 0) surface exposes bridging (O_{br}) and 3-fold coordinated (O_{3f}) oxygen as well as 5-fold coordinated

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Ru ions, typically referred to as coordinatively unsaturated sites, or Ru_{cus} [22]. Both experimental and computational evidence indicate that the stoichiometric surface can also accommodate additional oxygen at the cus sites, i.e., O_{cus} , and that the O_{cus} and O_{br} are the most labile and relevant to catalysis [27–29].

The CO_3^{2-} carbonate anion is trigonal planar and can in principle be formed by CO_2 adsorption at basic surface oxygen sites. We considered various CO_2 adsorption configurations at O_{cus} and O_{br} sites and identified two with negative formation energies relative to gas phase CO_2 . Fig. 1a shows that the most stable CO_2 adsorption site is at an O_{cus} site adjacent to a vacant cus site. CO_2 binds here in a bridge mode with an adsorption energy of -0.55 eV. The three O–C–O angles are identical (120°) and the upright C–O bond is slightly shortened with respect to the two bridge C–O. The adsorption energy is only slightly diminished by lateral interactions with neighbor adsorbates. O_{cus} /cus vacancy pairs are common on the oxygen-exposed RuO_2 surface [26,27].

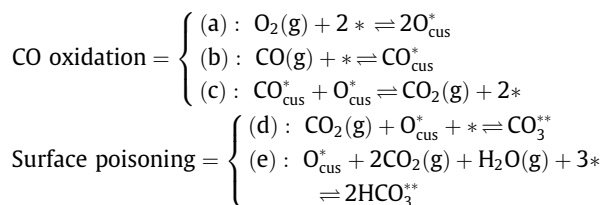
The next most stable configuration involves CO_2 binding at an O_{br} site with vacant neighbor cus site, forming the asymmetric carbonate shown in Fig. 1b. Trigonal symmetry is broken at this site and the three C–O bond lengths vary noticeably. The CO_2 adsorption energy increases to -0.35 eV, showing that O_{br} is somewhat less basic than O_{cus} . This species is consistent with the bidentate carbonate observed by exposure of CO_2 to the stoichiometric $\text{RuO}_2(110)$ surface at 175 K [18].

Bicarbonate (HCO_3^-) is the partially hydrated cousin of carbonate and has also been implicated in catalyst deactivation, for instance during CO oxidation over supported Au catalysts [30]. We explored various bicarbonate configurations on $\text{RuO}_2(110)$. The most stable binds on the cus row and derives from the cus row carbonate by addition of H to the apical O (Fig. 1c). The structure is typical of the planar bicarbonate anion, with a bent H–O–C fragment and two short C–O and one long C–OH bond. The O–Ru bond lengths increase 0.12 Å relative to the parent carbonate. The adsorption energy per $\text{HCO}_3^{*}_{\text{cus}}$ is -1.70 eV relative to gas phase CO_2 and H_2O , considerably more exothermic than the carbonate. It is worth noting that the bidentate carbonate Fig. 1a and bicarbonate structures Fig. 1c are both consistent with a recent experimental observation of carbon anions covering cus rows with 2-fold periodicity [19].

A bicarbonate can also be generated by H addition to the br–cus carbonate (Fig. 1d). Its structural details are similar to the cus bicarbonate but again distorted by the lower symmetry of the adsorption site. Its formation energy is calculated to be -1.46 eV per $\text{HCO}_3^{*}_{\text{br-cus}}$ relative to gas phase CO_2 and H_2O , slightly smaller than the cus bicarbonate.

Having identified the thermodynamically stable carbonate and bicarbonate structures, we now explore their contributions to the

surface poisoning observed in experiments [10,17,19]. We write a mean-field CO oxidation model including carbonate or bicarbonate poisoning as follows:



For simplicity, we only consider the participation of cus sites in CO oxidation, as the exact role of bridge sites has been under debate [9,31,32] and the cus-only model illustrates the important points. Including the less stable bridge–cus carbonate (Fig. 1b) and bicarbonate (Fig. 1d) configurations in the model has negligible effect on the results. The reaction energies are obtained through DFT calculations ignoring the variations due to oxygen coverage change: $\Delta E_1 = -1.84$ eV for oxygen adsorption reaction (a), $\Delta E_2 = -1.34$ eV for CO adsorption reaction (b), $\Delta E_4 = -0.55$ eV for carbonate formation reaction (d) and $\Delta E_5 = -3.40$ eV for bicarbonate formation reaction (e).

DFT calculations show that the barrier to O_2 dissociation (a) is only 0.25 eV with respect to chemisorbed O_2 and is barrierless relative to gas phase O_2 [26]. In contrast, using climbing image nudged elastic band (CI-NEB) calculations [33,34] we find the barrier to reaction (c) to be 0.90 eV, similar to previous reports [15]. The CO adsorption reaction (b) is barrierless relative to gas phase CO. We calculate the barrier to carbonate formation (d) to be only -0.10 eV relative to gas phase CO_2 , indicating that carbonate formation is facile. Bicarbonate likely forms via a multi-step process involving waters and possibly surface OH. For the purpose of modeling here we assume that the barriers to these processes are small enough to allow bicarbonate to form on the timescales of catalytic interest. Thus, we construct a model in which the CO oxidation reaction (c) is rate limiting and reactions (a), (b), (d) and (e) are in quasi-equilibrium.

The mean-field CO_2 formation rate then can be expressed as [10,35]:

$$R_{\text{CO}_2} = k_3 \theta_{\text{CO}} \theta_{\text{O}} (1 - \gamma^2) \quad (1)$$

where $k_3 = \nu e^{-E_a/k_B T}$, the prefactor ν takes a typical value of 10^{12} s^{-1} and E_a is 0.90 eV. The parameter $\gamma = P_{\text{CO}_2}^2 / (K_{\text{eq}} P_{\text{CO}}^2 P_{\text{O}_2})$ is the approach to equilibrium for the overall reaction stoichiometry ($\text{CO} + 2\text{O}_2 \rightleftharpoons 2\text{CO}_2$) and K_{eq} is the equilibrium constant of this overall reaction. θ_{CO} and θ_{O} are coverages of adsorbed CO and O, respectively, and can be determined by solving the site balance,

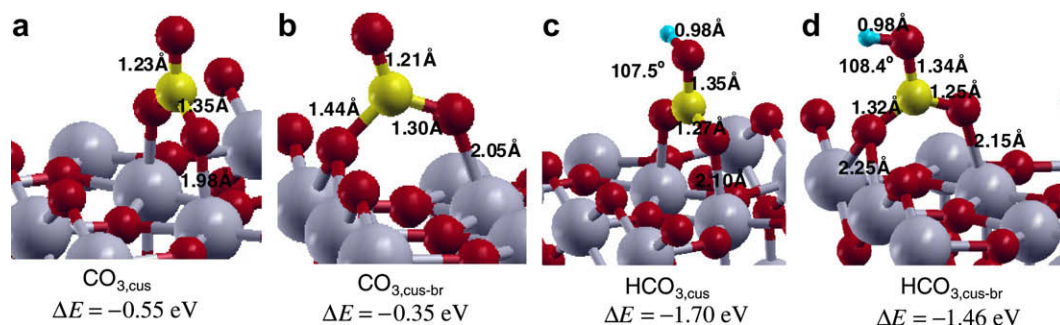


Fig. 1. Surface carbonate CO_3^{2-} and bicarbonate HCO_3^- adsorption configurations. (a) Bidentate carbonate along the cus row; (b) bidentate carbonate bridging br–cus row; (c) bicarbonate along cus–cus row; and (d) bicarbonate across br–cus. Adsorption energies shown are relative to gas phase CO_2 and H_2O . Red balls represent O, grey balls Ru, yellow balls C and blue balls H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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