Role of Magnetism in Catalysis: RuO$_2$ (110) Surface

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ABSTRACT: Angular momentum seems to not be conserved in chemical reactions where one of the reactants is magnetic; consequently, such reactions show a high activation barrier. An example is the production of hydrogen by electrolysis of water: practically all losses occur in the production of (magnetic) oxygen. Anodes with a low overvoltage (a measure of the losses) are based on the ruthenium dioxide (110) surface. First-principles electronic structure calculations show that this surface itself carries magnetic moments. This magnetic surface enables the production of oxygen in the ground state while conserving angular momentum.

INTRODUCTION

Electrolysis of water is a potential source of hydrogen on a large scale. A measure of the inefficiency in electrolysis is the overvoltage, the voltage needed to drive the process in excess of the voltage under thermodynamical equilibrium conditions. The contribution to the overvoltage of the oxygen evolution dominates overwhelmingly. One of the best anodes in this respect is based on the RuO$_2$ (110) surface, and improvements have been reported, such as, by the partial substitution of ruthenium by tungsten,$^1$ cobalt,$^2$ and nickel.$^3$

Because oxygen evolution produces magnetic oxygen from nonmagnetic water, the inclusion of the effects of surface magnetism could be highly relevant.$^4$ Because neither water nor hydrogen is magnetic, on a nonmagnetic anode the oxygen can be produced only in an excited nonmagnetic state without violating conservation of angular momentum. The two lowest excited states of the oxygen molecule are singlet states,$^1$ $^3\Delta_u$ and $^1\Sigma^+_g$ and $^1\Sigma^+_g$ 1 and 1.6 eV above the $^3\Sigma^+_g$ ground state.$^5$ For nonmagnetic anodes, we associate the high overvoltage with the notion that oxygen is produced initially in its nonmagnetic excited state and decays slowly to the ground state by higher order processes. A detailed study of the energetics of the oxygen evolution on the RuO$_2$ (110) surface was reported by Rossmeisl et al.$^6$

Here we report on the local electronic and magnetic properties of RuO$_2$ (110) surfaces. We show that the RuO$_2$ (110) surface is magnetic. This is an unexpected property because the bulk RuO$_2$ is not magnetic. Magnetism in 4d and 5d metals and their compounds is rare but not unique$^7$ for example, magnetic properties of RuO$_2$ nanoparticles have been investigated.$^{10,11}$ The surface magnetism that we report here is an important property because it provides us the necessary degree of freedom to allow the production of oxygen in its magnetic ground state while conserving angular momentum.

DETAILS OF THE CALCULATIONS

Experimental$^{12−15}$ and theoretical analyses$^{16−24}$ show that the RuO$_2$ (110) surface has two different ruthenium atoms, one with six-fold coordination by oxygen (Ru6) and one with a five-fold coordination (Ru5). The latter is regarded as the active site in catalysis.$^{12−24}$ Previous studies have focused on surface morphologies and local atomic structure. Scheffler et al. found that the clean surface exists in an oxygen-poor environment, whereas in an environment rich in oxygen the stable form of the RuO$_2$ (110) surface has terminal oxygen on top of the Ru5 atoms.$^{19−22}$

RuO$_2$ can be regarded as consisting of alternate layers of oxygen and RuO$_2$ layers along the (110) direction. We cleave the crystal in the O atomic layer; a surface oxygen atom bridges two Ru6 atoms. There are two distinct ruthenium atoms in the (110) surface: a six-fold-coordinated (Ru6) and a five-fold-coordinated (Ru5), as shown in Figure 1a. A unit cell of 3.14 Å $\times$ 6.43 Å $\times$ 25.00 Å containing 24 atoms in 9 atomic layers in a slab and 12 Å vacuum between them was employed.

Calculations were carried out using the first-principles code Vienna ab initio simulation program (VASP)$^{25−28}$ employing density functional theory (DFT), and the projector-augmented wave (PAW) method.$^{29,30}$ The generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE)$^{31,32}$ was employed for the exchange and correlation potentials. The quantization axis for the spin is taken along the z direction. The Brillouin-zone integration used 8 $\times$ 8 $\times$ 12 k-mesh or 105 k-points in the irreducible Brillouin zone (BZ) of bulk RuO$_2$. For the (110) surface systems the electronic wave functions were sampled on 12 $\times$ 6 $\times$ 1 k-mesh or 28 k-points in the irreducible BZ. The cutoff energy of the wave functions was 500 eV. The cutoff energy of the augmentation function was 605 eV, and for the smearing we used Gaussian method. The structure was

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optimized until all forces were smaller than 0.01 eV/Å. The convergences of the cutoff energies and k-meshes have been verified.

■ CLEAN RuO2 (110) SURFACE

The results of structural relaxations of bulk RuO2 are in line with former calculations;33,34 see Table 1. Calculations for the relaxed RuO2 (110) surface using the spin-polarized DFT-GGA method resulted in a magnetic solution 38 meV lower in total energy compared with the nonmagnetic solution. The spin-polarization is confined to the surface atoms: 0.60 $\mu_B$ for Ru6, −0.24 $\mu_B$ for Ru5, and 0.19 $\mu_B$ at the bridging oxygen site (O2). (See Table 2.) The total magnetization of each surface of the slab is 0.55 $\mu_B$. Figure 2 reveals the origin of the surface magnetism: it shows the partial density of the surface ruthenium 4d and oxygen 2p states around the Fermi level for both nonmagnetic and the magnetic cases. Both nonmagnetic densities of states reach the Fermi level for the nonmagnetic and the magnetic cases. The shape of the partial density of the surface ruthenium 4d states is significantly different from that of the bulk due to a different crystal field splitting.

The O2 2p states have a density of ∼0.80 states/eV per atom, which is significantly larger than those in the subsurface layer and bulk (typically around 0.2 states/eV per atom). Calculations show a spin splitting of about 0.8 eV with a peak at about −0.3 eV for the spin-up electrons and another peak at about 0.5 eV for the spin-down electrons. As a result, there is a magnetic moment of ∼0.19 $\mu_B$ at the bridging oxygen site. The spin-polarization shows little effect on the subsurface O atoms.

Table 2. Surface Energy and Local Moments of RuO2 Rutile (110) and (110)-O Surfaces Using the DFT-GGA Method

<table>
<thead>
<tr>
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<th>present</th>
<th>literature</th>
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<tbody>
<tr>
<td>$\mu_B$</td>
<td>E_{surf} (J/m$^2$)</td>
<td>$E_{sp}$- $E_{nm}$ (meV/cell)</td>
</tr>
<tr>
<td>(110)</td>
<td>1.04</td>
<td>−38</td>
</tr>
<tr>
<td>(110)-O</td>
<td>1.14, 1.03</td>
<td>−53</td>
</tr>
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Figure 1. Local coordination and the spin density of the RuO2 (110) surfaces. Blue corresponds to negative; red corresponds to positive spin density. (a) Bridging O (O2) atoms, six-fold-coordinated Ru atoms (Ru6), and five-fold-coordinated Ru atoms (Ru5). (b) Surface with oxygen coverage: the Ru5 covered by one O (O1). The numbers represent the Ru–O bond lengths (in angstroms).

Figure 2. Partial density of states of the surface O and Ru states on RuO2 (110) showing the effect of spin polarization. Remark the maxima at the Fermi energy for several nonspin-polarized cases.
Because surface magnetism is a subtle effect, we also performed WIEN2k\(^{38}\) calculation for clean RuO\(_2\) (110) surface to make a benchmark. We chose Wien2k for benchmarking because WIEN2k and VASP are different DFT methods. WIEN2k is a full potential linearized augmented plane wave (LAPW) method where VASP is a plane-wave pseudopotential method. For WIEN2k calculations, a 3.14 Å × 6.43 Å × 25.00 Å unit cell was used that contains 24 atoms in 9 atomic layers and also more than 12 Å vacuum. This is the same unitcell that we used in VASP calculations. The electronic wave functions were sampled on 12 × 6 × 1 k-mesh or 18 k-points in the irreducible BZ using the Monkhorst-Pack method.\(^{39}\) To make a reasonable comparison between these two different methods, we optimized the cell with WIEN2k and used the optimized geometry as a starting guess for VASP. For relaxation in VASP, we used the same parameters, for example, convergence criteria, k-point generation scheme, and atomic radii for local magnetic moments, as we used in WIEN2k. Finally, we observed that the relaxed geometries for VASP and WIEN2k are almost the same and total magnetic moments per surface unit cell for VASP and WIEN2k are close to each other, 0.56 and 0.52, respectively, which we consider to be a good agreement. So, WIEN2k calculations confirmed that the RuO\(_2\) (110) surface is magnetic.

### O-COVERED RuO\(_2\) (110) SURFACE

The addition of oxygen on top of Ru5 (Figure 1b) has a profound influence; see Table 2. The Ru5 shifts 0.09 Å outward, in contrast with the clean surface, where it moved 0.07 Å inward. The new Ru–O bond is short, 1.73 Å, on the expense of the Ru–O bond to the oxygen below, which expands from 1.90 Å in the clean surface to 2.08 Å in the case of an extra oxygen. The addition of an oxygen atom on top of the Ru5 atom slightly perturbs the local coordination of the Ru6 atom. The Ru6 atom and the bridging O atom move slightly inward. The magnetic ground state is more stable by 53 meV compared with the nonmagnetic case, which is 15 meV more compared with the case without oxygen coverage.

Figure 3 shows the calculated partial density of the ruthenium 4d and oxygen 2p states at the oxygen-covered surface. The peak positions and widths of the densities of states of the Ru6 4d and the bridging O 2p states are basically the same as those of the clean surface. For the nonmagnetic case, the density of states peaks at the Fermi level for both the ruthenium 4d and oxygen 2p states, and it is mostly due to the oxygen 2p states (as it does for the clean surface). Spin-polarization has a significant influence on these partial densities of states.

The partial density of the Ru5 4d states of the oxygen-covered surface has a significant different shape as compared with that of the clean surface (Figures 2 and 3). There are two strong peaks at about −1.0 and +0.4 eV. The latter peak corresponds to the peak from the 2p states of the terminal oxygen atom. Spin-polarization has much less influence on the Ru5 4d and terminal O (O1) 2p states. The magnetic moments of the Ru6 and Ru5 are parallel, in contrast with the case of the clean surface.

On the oxygen-covered RuO\(_2\) (110) surface, the local magnetic moments of the Ru6 and bridging O atoms are close to those for the clean surface. The moment of the Ru5 on the oxygen-covered surface remains very small (~0.1 \(\mu_B\)) but aligns parallel. Therefore, the total magnetic moment of the oxygen-covered surface increases to 1.22 \(\mu_B\) per unit cell on one oxygen-covered surface and from 0.55 \(\mu_B\) per unit cell on a clean (110) surface.
We performed two different sets of calculations that we named “Singlet” and “Triplet”. In the “Singlet” case, we assumed that the RuO$_2$ (110) surface is not magnetic so the O$_2$ molecule should be produced initially in its nonmagnetic singlet excited state. For this scenario, we obtained the total energy difference between these two states from nonspin-polarized DFT calculations and labeled it as “Singlet” in Figure 4. For the “Triplet” case, surface magnetism enables the production of oxygen in its magnetic ground state. First, we performed spin-polarized DFT calculation to find the local and total magnetic moments of the initial state (Table 3). Then, we fixed the total spin angular momentum of the unitcell and tried to obtained O$_2$ molecule in its triplet magnetic ground state for the final step. We observed that surface atoms rearrange their moments to conserve total spin angular momentum in the unitcell while obtaining O$_2$ molecule in its magnetic ground state. We also observed that the total energy change in the “Triplet” case is ~1 eV lower in energy than the “Singlet” case, which can be seen in Figure 4.

## Conclusions

Magnetism usually occurs in materials containing elements where a certain angular momentum appears first. The orthogonality of the valence electrons (that carry the magnetic moment) to the core is always fulfilled, so no constraints exist on the radial Schrödinger equation (any constraint increases the energy and hence the delocalization of these states), but several exceptions exist; for example, strontium ruthenate is ferromagnetic. In general, surfaces with atoms with a lower coordination show an increased tendency toward magnetism. Magnetism is the rule rather than the exception in isolated atoms, but also isolated 4d atoms in an alkali–metal matrix show local moments.

The calculations presented here show that both the (110) stoichiometric and the oxygen-covered surfaces of ruthenium-dioxide show local magnetic moments. The relevance of the surface magnetism reported in this article is in electrolysis, so how surface magnetism can be important for electrolysis of water is also illustrated.

The spin-conservation rule (which we call angular momentum conservation) is a key selection rule for chemical reactions. The importance of the spin-selection rule can be seen in Scheffler’s work. They concluded the origin of the low sticking parameter of O$_2$ on Al(111) is having O$_2$ in a triplet and the Al(111) surface in a singlet state. Another example is a polynuclear, magnetic cluster containing four manganese ions. A second magnetic entity seems ubiquitous in the production of molecular oxygen.

## References