

Mechanism for Oxidative Dissolution of a Cr Atom from a Pt Surface: Molecular Orbital Theory

Alfred B. Anderson*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7078

Paul Shiller

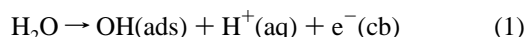
DELPHI Packard Electric Systems, PO Box 431, Warren, Ohio 44486

Received: October 1, 1997; In Final Form: February 4, 1998

A molecular orbital study has been made of the oxidative abstraction of a substitutional surface Cr atom from the Pt(111) surface. The overall process studied is $\text{Cr}(\text{subst}) + 4\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}\cdot\text{CrO}_3(\text{g}) + 6\text{H}(\text{ads})$ (i). When solvated, the $\text{H}_2\text{O}\cdot\text{CrO}_3$ molecule is expected to rearrange to $\text{H}_2\text{CrO}_4(\text{aq})$, and the adsorbed H atoms will be discharged to form $\text{H}^+(\text{aq})$ plus electrons that enter the anode. The latter steps, which are not expected to be kinetically limiting, were not studied. The mechanism explored for forming $\text{H}_2\text{O}\cdot\text{CrO}_3$ is one of sequential bonding of H_2O to Cr and dehydrogenation, leading to strongly adsorbed $\text{Cr}(\text{OH})_3(\text{ads})$. A water molecule bonds, forming $\text{H}_2\text{O}\cdot\text{Cr}(\text{OH})_3(\text{ads})$ which then loses three hydrogen atoms to the surface. The product, $\text{H}_2\text{O}\cdot\text{CrO}_3(\text{ads})$, is weakly held and desorbs easily. Each step leading to the product in eq i is calculated to have a low activation energy. However, $\text{HCrO}_4^-(\text{aq})$ remains stable only when the electrode is at a potential >1.35 V (SHE); otherwise, it is expected to be reduced to $\text{Cr}^{\text{III}}(\text{aq})$ as it desorbs.

Introduction

Platinum, as an anode for oxidation of hydrogen, methanol, and other hydrocarbons in fuel cells, becomes poisoned by carbon monoxide at potentials less than 0.8 V (SHE).^{1,2} At potentials greater than this, the $\text{CO}(\text{ads})$ is rapidly oxidized. The 0.8 V potential also marks the onset of Pt surface oxidation by water decomposition,^{2,3} and on this basis it was suggested that the water decomposition product is the oxidant of $\text{CO}(\text{ads})$. The oxidant has been proposed to be $\text{OH}(\text{ads})$ formed according to

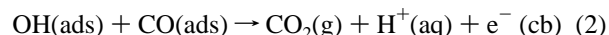


where the electron is carried away in the conduction band (cb). Theory has supported this possibility by demonstrating that the activation energy for breaking an O–H bond in an adsorbed water molecule decreases as the surface is made a better electron acceptor, that is, more positive.⁴

For clean Pt(111), structural changes occur at potentials greater than the 0.8 V onset potential for water decomposition on the surface.⁵ At about 1.2 V, surface Pt atoms evidently move, resulting in roughening. The nature of the adsorbed oxygen species associated with roughening, whether $\text{O}(\text{ads})$ or $\text{OH}(\text{ads})$, is not established. The roughening process is irreversible: after cycling the potential to less positive values, to reduce the oxygen species, the cleaned surfaces remained rough. At potentials less than 1.2 V any surface Pt atom motion that may occur is reversible upon reduction.

Anodic dissolution of alloying transition metals on⁶ and in⁷ Pt has been observed. Platinum–ruthenium alloys have been particularly well studied because they activate removal of the $\text{CO}(\text{ads})$ poison reducing the onset potential to about 0.6 V.^{2,8} Theory has shown that a substitutional Ru atom in the Pt(111) surface will attract H_2O and greatly lower the activation energy for $\text{OH}(\text{ads})$ formation by reaction 1.⁹ It was furthermore shown

that once $\text{OH}(\text{ads})$ forms on these sites, it is able to release it to oxidize $\text{CO}(\text{ads})$ on an adjacent Pt site:



This provided good support for the notion that $\text{OH}(\text{ads})$ formation by eq 1 is the first step in water oxidation on pure and alloyed Pt surfaces. Ruthenium atoms in Pt alloy electrode surfaces undergo anodic dissolution beginning at about 0.75 V.² Nothing is yet known about the mechanism beyond the proposed first step of Ru–OH bond formation at 0.6 V.

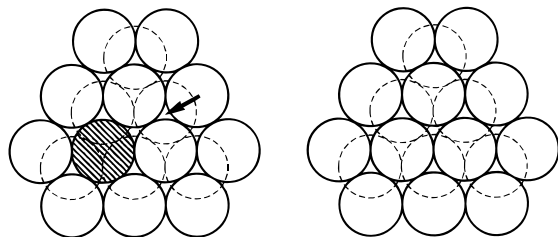
Molecular orbital theory predicted that a number of other electropositive metal atoms in addition to Ru may activate the forming of $\text{OH}(\text{ads})$ at potentials significantly lower than on pure Pt.¹⁰ Chromium is particularly interesting because of its predicted very low $\text{OH}(\text{ads})$ generation activation energy (0.08 eV) when present substitutionally in Pt,¹⁰ suggesting that it could be an alternative to Ru in fuel cell anode applications, and because it appears to activate the O_2 reduction capability of Pt fuel cell cathodes.¹¹ Interestingly, Cr is found to dissolve readily from Pt–Cr alloy anodes in acidic solution, generating roughened surfaces.¹²

It is, as far as we know, not yet known whether Pt–Cr alloys are active for fuel cell anode applications. For cathodes, which typically operate at about 0.3 V overpotential, which is about 0.9 V,¹³ the activation has been proposed to be due to the increased electrode surface area that comes with roughening¹² or by electronic, geometric, and chemical factors of the alloy.¹¹

With this background it is of interest to probe the dissolution process of Cr in Pt–Cr alloys by any available means. We have taken a theoretical route, examining the subsequent reactions of CrOH in a Pt anode surface with H_2O molecules to form Cr^{III} in the form of $\text{Cr}(\text{OH})_3$ and Cr^{VI} in the form of $\text{H}_2\text{O}\cdot\text{CrO}_3$, which is expected to rearrange to $\text{HCrO}_4^-(\text{aq}) + \text{H}^+(\text{aq})$.

TABLE 1: Parameters Used in the Calculations: Principal Quantum Numbers, n , Diagonal Hamiltonian Matrix Elements, H (eV), Orbital Exponents, ζ (au), and Linear Coefficients, c , for Double- ζ d Orbitals

atom	s			p			d					
	n	H	ζ	n	H	ζ	n	H	c_1	ζ_1	c_2	ζ_2
H	1	12.1	1.2									
O	2	26.98	2.146	2	12.12	2.1270						
Cr	4	8.265	1.6	4	5.376	1.3	3	9.75	0.50581	4.95	0.67471	1.8
Pt	6	10.5	2.554	6	6.460	2.25	5	11.10	0.65581	6.013	0.57150	2.396

**Figure 1.** CrPt₁₇ and Pt₁₈ cluster models of the Pt(111) surface. The arrow on the CrPt₁₇ cluster indicates the 3-fold site to which CrOH is moved as discussed in the text.

Theoretical Method

The semiempirical atom superposition and electron delocalization molecular orbital (ASED-MO) theory¹⁴ has been used for this study. Standard atomic parameters were employed for the Pt atoms, and these correspond to a potential of about 0.6 V on the SHE scale, based on the potential of zero charge at pH = 0.¹⁵ All parameters are the ones used in previous studies including those listed above;^{4,9,10} they are presented in Table 1. A standard two-layer-thick 18-atom cluster model was used to represent the pure and alloyed Pt(111) surface as shown in Figure 1. For the 18-metal atom clusters, eight orbitals at the top of the doubly occupied band were assigned single occupation. When radical adsorbates were present, nine orbitals were assigned half occupation. Our calculated reaction activation energies are approximate but they are sensitive to structure factors, and this sensitivity provides our basis for analysis. For H₂O(ads) decomposing to H(ads) and OH(ads) on Pt(111) a previous calculation yielded an activation barrier of 0.44 eV,⁴ which is reasonable.

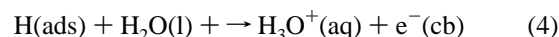
Results and Discussion

Motion of Cr from the Surface Substitutional Site to a Chemisorbed Site. Cr was calculated to relax 0.61 Å into the surface, and this relaxed structure was used for the initial alloy structure in the following calculations. Once OH was formed by dehydrogenation of H₂O on the Cr site, the Cr atom relaxed up to a position of 0.45 Å below the surface plane. In this site, Cr was protected by OH, becoming inaccessible by water molecules for further oxidation. The next step was motion of CrOH to a site on the surface using the alloy cluster model in Figure 1. A series of calculations showed that CrOH bonded most strongly on a 3-fold surface site, when constrained to be perpendicular to the surface plane of the Pt₁₈ cluster. Ten evenly spaced lateral displacements between the substitutional site and the adjacent 3-fold top site were selected for calculations, and full optimization of the CrOH structure at each of these lateral positions was performed. The CrOH lifted up over the 2-fold bridging site at a height of 1.62 Å and then dropped into the 3-fold site with a final height of 1.56 Å. Over this path the system increased its stability 2.30 eV with no intervening barrier. The adsorbed CrOH molecule was now in a position open for attack by H₂O molecules. All further calculations were made with the CrOH and its oxidation products over the center 3-fold site of the Pt₁₈ cluster shown in Figure 1.

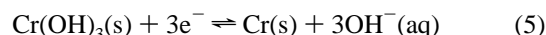
Oxidation of CrOH(ads) by H₂O. An H₂O molecule was calculated to bond to CrOH(ads) at the 3-fold surface site with 2.37 eV stability, which was almost as great as calculated for H₂O bonding to the substitutional surface Cr atom. The adsorbed HOCrOH₂ had a planar structure, with an OH bond in H₂O directed toward the surface, which was appropriate for hydrogen transfer to the surface. This structure was stabilized by a π -allylic delocalization involving the p lone-pair orbital on the H₂O molecule. For the net reaction



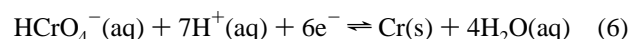
the calculated activation barrier, based on stretching the OH bond in 0.1 Å increments and optimizing the other structure variables of the surface complex, was 0.43 eV. At positive potentials, including the anodic dissolution range, H(ads) will be oxidized:



An H₂O molecule was calculated to bond to Cr(OH)₂(ads) with a stability of 1.63 eV, and the activation barrier for its dehydrogenation was calculated to be 0.60 eV. The product, Cr(OH)₃(ads), bonded most stably to the 3-fold site through Cr. The three OH were not in a good orientation for bond scission, being directed away from the surface. Exploration of stretching one of them indicated that the activation barrier would be greater than 1.0 eV. Solid Cr(OH)₃ is stable in basic solution at potentials greater than -1.48 V¹⁶ according to



The calculated adsorption energy for Cr(OH)₃ was high, 5.72 eV over the 3-fold site of Pt(111), but very strong acid might remove it as Cr³⁺(aq). Further reaction with water was considered next. An H₂O molecule was found to bond to the Cr in Cr(OH)₃(ads), causing an inversion with no activation barrier, forcing the three OH bonds to become directed toward the surface, which activated them. The total stabilization for this process was 1.80 eV. Sequential dehydrogenation of adsorbed H₂O·Cr(OH)₃ was examined next. Activation barriers for the first, second, and third H transfer from O to the neighboring Pt atoms were calculated to be relatively small, 0.16, 0.16, and 0.64 eV, respectively. Structures for the various intermediates are shown in Figure 2. The resulting H₂O·CrO₃-(ads) had Cr fully oxidized, and it bonded only weakly to the surface by lone-pair donation from the three O to the surface Pt atoms. The desorption energy for this complex was calculated to be small, 0.25 eV, so it can now desorb. Rearrangement to form H₂CrO₄ or HCrO₄⁻ is expected to be catalyzed by bridging water molecules. This might be the mechanism for the fairly low (0.606 V) reversible potential Cr⁰, Cr⁶⁺ equilibrium:



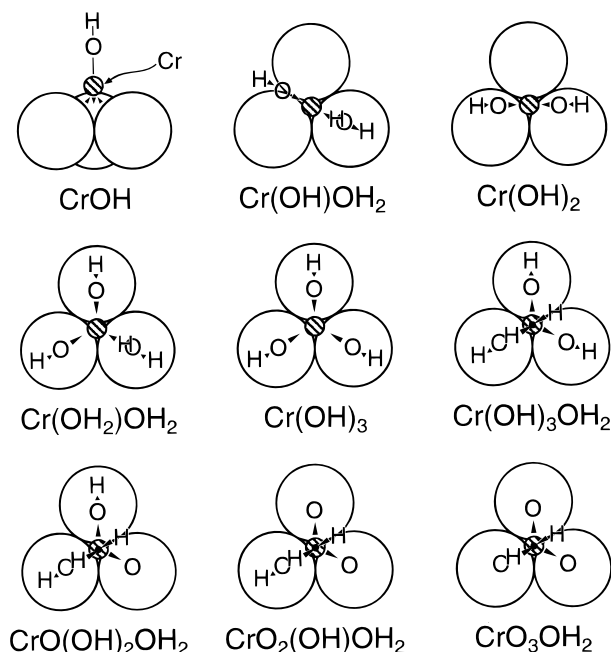
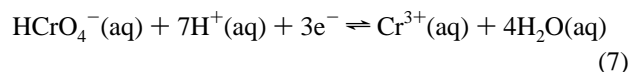


Figure 2. Structures of the intermediates bound to Pt_{18} as discussed in the text.

However, HCrO_4^- (aq) is a strong oxidant in acid solution:



with a reversible potential of 1.350 V. Because of this, as the hydrated CrO_3 desorbs it should undergo reduction to Cr^{3+} when the potential is less than 1.350 V, but greater than -0.744 V.

Finally, it is noted that our calculations predict that PtOH , once formed by oxidation of $\text{H}_2\text{O}(\text{ads})$, also, like CrOH , becomes more stable (by 1.20 eV) when it leaves the surface to move to a 3-fold adsorption site. Since PtOH forms at a higher potential than CrOH ,⁵ it is possible to propose that it is held in the surface because the surface sites are blocked by strongly adsorbed H_2O and by $\text{OH}(\text{ads})$ on adjacent sites. At high potential $\text{OH}(\text{ads})$ deprotonates and the surface restructures, according to ref 5.

Concluding Comment

The effects of electrode potential have not been modeled in the present study but from past work,^{4,9} it is expected that the

main result of increasing the potential would be reducing the OH bond scission activation energy barriers. The third water molecule bond scission had the highest barrier in the case of forming $\text{Cr}(\text{OH})_3(\text{ads})$ and would be rate limiting for its formation. This species bonds strongly to the Pt surface and might play a role in passivating it. Breaking the third OH bond in $\text{Cr}(\text{OH})_3(\text{ads})$ is calculated to be the slow step in forming weakly held $\text{H}_2\text{O} \cdot \text{CrO}_3(\text{ads})$, and its barrier is larger than that for the slow steps in $\text{Cr}(\text{OH})_3(\text{ads})$ formation, so a higher potential will be needed for $\text{H}_2\text{O} \cdot \text{CrO}_3(\text{ads})$ formation. Once it begins to desorb, it will be reduced back to a $\text{Cr}^{\text{III}}(\text{aq})$ species if the electrode potential is less than about 1.35 V, which seems to be the case for some studies of anodic dissolution of Cr from the Pt–Cr alloys.¹²

Acknowledgment. This work was funded by ARPA through ONR Contract N0014-92-J-1848.

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