

Chlorination of zirconium (0001) surface: A first-principles study

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Abstract

The mechanisms and energetics of Zr(0001) surface chlorination by dissociative adsorption of gaseous Cl₂, and associated speciation and surface degradation processes, have been investigated within the framework of density functional theory. Chlorination of Zr(0001) is predicted to be exothermic by ~3 eV/Cl for dissociative adsorption of a single Cl₂ molecule, followed by exothermic chlorination to 1ML and 2 ML under Cl-rich conditions, with respective energy gains of 1.93 and 2.79 eV/Cl. Calculations also show that exfoliation of the top Cl–Zr–Cl sandwich layers is exothermic and most energetically favorable, and can thus be considered as a leading mechanism for Zr(0001) surface dissolution. Consistent with experimental findings, formation of ZrCl₄ molecular products is also found to be dominant during Zr(0001) chlorination.

Keywords:

1. Introduction

Chemisorption of halogen atoms on metal surfaces is often considered as prototypical to gain fundamental and applied understanding of adsorption-specific electrochemical systems (1, 2). Despite the apparent simplicity of such systems, an accurate experimental characterization of the oxidation state of adsorbed species produced from the reaction of halogens with metal surfaces is often difficult (2). In particular, this is the case for reaction products obtained from the dissolution of metals surfaces exposed to chlorine gas.

The formation of volatile chloride species upon chlorination of complex metal ores plays a crucial role in the industrial production and purification of metals such as zirconium or titanium *via* the Kroll reduction process (3, 4, 5). Chlorination can also be used advantageously for large-scale separation and recovery of metals contained in scrap material by conversion to their respective chlorides, as demonstrated, for example, in recent studies aiming at recovering/recycling zirconium from U–Zr alloys or used nuclear fuel cladding (6, 7, 8).

In this Letter, the mechanisms and energetics of Zr(0001) surface chlorination and associated specia-

tion and surface degradation processes have been studied using density functional theory (DFT), in order to gain insights into the purification processes of Zr-based cladding materials by chlorination. Details of our computational approach are given in the next section, followed by a discussion of our results.

2. Computational methods

First-principles total energy calculations were carried out using DFT, as implemented in the Vienna *ab initio* simulation package (VASP) (9). The exchange-correlation energy was calculated using the generalized gradient approximation (GGA), with the parameterization of Perdew, Burke, and Ernzerhof (PBE) (10). Standard functionals such as the PBE or PW91 functionals were found in previous studies to correctly describe structures and properties of zirconium and its alloys and transition-metal chloride compounds (11, 12, 13, 14, 15).

The interaction between valence electrons and ionic cores was described by the projector augmented wave (PAW) method (16, 17). The Zr(4*p*⁶, 5*s*², 4*d*²) and Cl(3*s*², 3*p*⁵) electrons were treated explicitly as valence electrons in the Kohn-Sham (KS) equations and the remaining core electrons together with the nuclei were represented by PAW pseudopotentials. The KS equation

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was solved using the blocked Davidson iterative matrix diagonalization scheme (18). The plane-wave cutoff energy for the electronic wavefunctions was set to 500 eV, ensuring the total energy of the system to be converged to within 1 meV/atom. Electronic relaxation was performed with the conjugate gradient method accelerated using the Methfessel-Paxton Fermi-level smearing (19) with a Gaussian width of 0.1 eV.

Ionic and cell relaxations of bulk α -Zr were carried out simultaneously, without symmetry constraints applied, using the quasi-Newton algorithm and the Hellmann-Feynman forces acting on atoms were calculated with a convergence tolerance set to 0.01 eV/Å. The Brillouin zone (BZ) was sampled using the Monkhorst-Pack k -point scheme (22) with a k -point mesh of $11 \times 11 \times 7$ for the bulk structure. The tetrahedron method with Blöchl corrections was used for BZ integrations (23). A (2×2) surface slab model was constructed by cleaving the optimized α -Zr bulk structure along the lowest-energy, (0001) basal plane. A vacuum region of ~ 20 Å along the z -axis normal to the surface was introduced between periodic slabs. A $3 \times 3 \times 1$ k -point mesh was used for BZ integrations for all surface slab models. The bottom row of Zr atoms in the slab was kept fixed in relaxation calculations to simulate the α -Zr bulk limit.

3. Results and discussion

The computed lattice constants of hexagonal close-packed bulk α -Zr (space group $P6_3/mmc$; IT No. 194; $Z = 2$) are $a = 3.24$ Å and $c = 5.15$ Å ($c/a = 1.59$), in excellent agreement with the experimental values of $a = 3.2331$ Å and $c = 5.1491$ Å ($c/a = 1.5926$) (20).

Figure 1 illustrates the dissociative adsorption of a Cl_2 molecule on Zr(0001) surface and associated energetics predicted from DFT calculations. The computed Cl–Cl bond distance increases from 2.03 Å for an isolated Cl_2 molecule far from the surface [$d(\text{Cl} - \text{Zr}) \geq 4.5$ Å] to 3.29 Å as it approaches the Zr surface [$d(\text{Cl} - \text{Zr}) \leq 2.5$ Å], thus indicating the occurrence of Cl_2 dissociation at the surface. The computed bond length of an isolated Cl_2 molecule is close to the experimental value of 1.987 Å for its electronic ground state $X^1\Sigma_g^+$ (21).

In order to represent realistic experimental chlorination conditions occurring under Cl_2 -rich atmosphere, reactivity of Cl_2 on Zr(0001) was also investigated with up to 2 ML coverage as shown in Figure 2. A total of four Cl_2 molecules were introduced on top of the Zr(0001) slab surface models (c.f. Figure 2). Chlorination of Zr(0001) is predicted to be exothermic, with an energy gain of ~ 3 eV/Cl when one Cl_2 molecule approaches

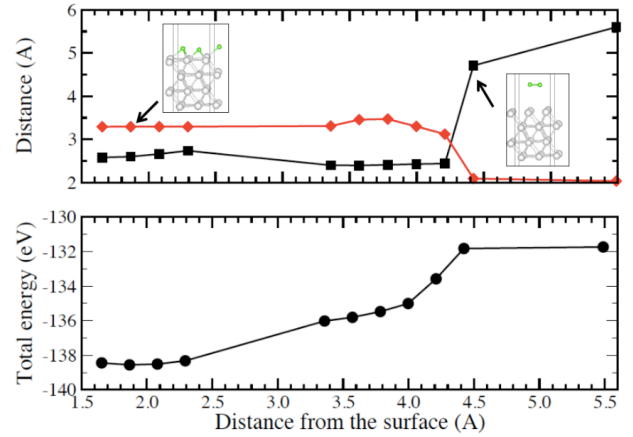


Figure 1: Dissociative adsorption of a single $\text{Cl}_2(\text{g})$ on Zr(0001) surface. *Top*: calculated Cl–Cl (red) and Cl–Zr (black) distances; *Bottom*: total energy profile with respect to the distance between Cl atoms and the surface. The distances and energy are in expressed in angstroms and eV, respectively. Color legend: Cl, green; Zr, grey.

Zr(0001) as discussed above. Under Cl-rich conditions, further exothermic chlorination to 1ML followed by 2 ML are expected, with energy gains of 1.93 eV/Cl and 2.79 eV/Cl, respectively.

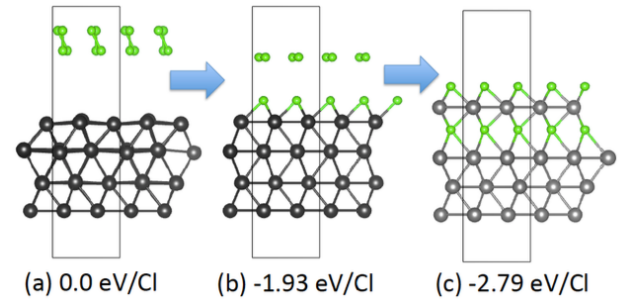


Figure 2: Chlorination of Zr(0001) surface: (a) no Cl atoms on the Zr (0001) surface, (b) 1ML of Cl atoms on the surface, and (c) 2 ML of Cl atoms sandwiching the top-most Zr monolayer. Color legend: Cl, green; Zr, grey.

Once chlorination occurs, the surface chemistry of Zr(0001) will be altered significantly, resulting in the formation of new compounds (e.g., ZrCl , ZrCl_2 , ZrCl_3 , and ZrCl_4) and/or eventually leading to complete surface dissolution. Therefore, additional theoretical calculations were aimed at identifying the most probable dissociating Zr–Cl species. As a first step, the possible exfoliation process of the top-most layers of chlorinated Zr(0001) slab surface was investigated, as shown in Figure 3. Process (a) in Fig. 3, which corresponds to the

loss of all the surface Cl atoms, is energetically unfavorable due to its large energy penalty (~ 1.89 eV/Cl). Process (b), which simulates the exfoliation of two surface layers, i.e. the surface Cl atoms along with the top Zr atoms, is slightly more probable with a smaller energy penalty of ~ 0.17 eV/Cl than process (a). Process (c) corresponding to the exfoliation of the top three layers consisting of Cl–Zr–Cl sandwich structures is exothermic, thus most probable. Therefore it is found that chlorination can facilitate the dissolution by cleavage of Cl–Zr–Cl layers from Zr(0001).

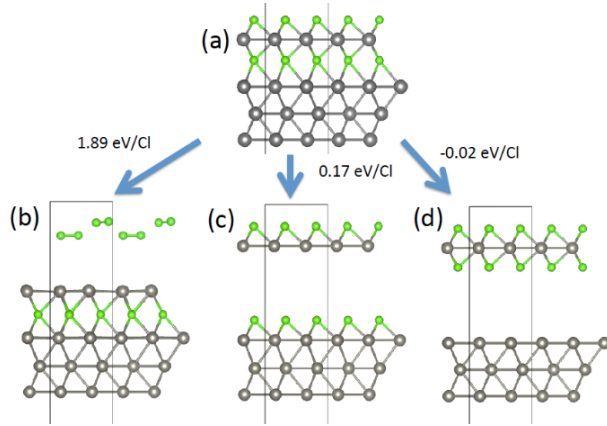


Figure 3: Cleavage of Zr–Cl species from Zr(0001) surface: cleavage of (a) the top layer only, (b) the top two layers (1st and 2nd), and (c) the top three layers. Color legend: Cl, green; Zr, grey.

As shown above (cf. Figure 2), chlorination up to 1ML is rather straightforward, resulting in energy gain of 1.93 eV/Cl as depicted in Fig. 2(b). However, chlorination up to 2MLs as represented in Fig. 2(c) requires an additional diffusion process of Cl into the subsurface of Zr(0001). Therefore, DFT calculations were carried out to investigate the energy barrier when a Cl atom or Cl atoms diffuse into the Zr metal system. Two possible scenarios were tested for the Cl diffusion process into the subsurface of Zr(0001): (i) a single Cl atom diffusing into the bare Zr metal surface; (ii) a Cl atom diffusing into the 1ML-Cl covered Zr(0001) surface. In the case of the bare metal surface, the Cl atom has to overcome a large energy barrier of ~ 3 eV when it goes through the surface Zr atoms, as shown in Figure 4(a). In the case of a Cl atom moving into the 1ML-Cl covered Zr (0001), a large energy barrier of ~ 2.6 eV is present when it diffuses through surface Zr atoms (see Figure 4(b)). The energetic bottleneck for a Cl atom to diffuse into the subsurface is to pass through the surface Zr atoms for both bare and 1ML-Cl covered Zr(0001).

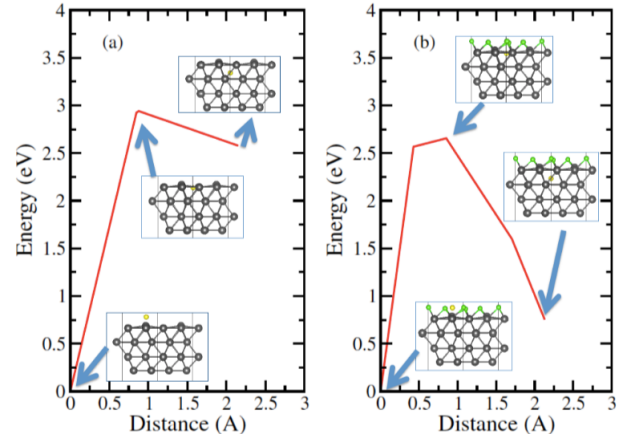


Figure 4: Diffusion of a Cl atom into: (a) the bare Zr metal surface and (b) the 1ML-Cl covered Zr(0001) surface. Color legend: Cl, green; Zr, grey. The yellow sphere indicates the Cl atom that diffuses into the metal system. The reference was taken when a Cl atom is 3 Å above the Zr (0001) surface.

The energy barrier is only slightly smaller for the 1ML-Cl covered surface compared to the case of Cl diffusion through the bare metal surface.

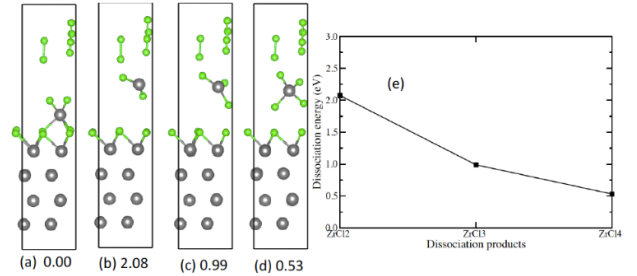


Figure 5: Ball-and-stick models of (a) chlorination of Zr(0001) and dissociation of (b) ZrCl_2 , (c) ZrCl_3 , and (d) ZrCl_4 , and (e) their corresponding calculated dissociation energies. The energy of (a) is taken as reference. The unit of the energy is in eV. Color legend: Cl, green; Zr, grey.

Finally, possible dissociation mechanisms of zirconium chlorides such as ZrCl_2 , ZrCl_3 and ZrCl_4 were also assessed using DFT models displayed in Figure 5, in terms of their respective dissociation energies. The computed dissociation energies of ZrCl_2 , ZrCl_3 and ZrCl_4 molecular species from the Zr(0001) surface were 2.08, 0.99 and 0.53 eV, as summarized in Figure 5. The energy of the geometry before dissociation shown in Figure 5(a) was taken as a reference. Consistent with experimental findings, ZrCl_4 molecular species are en-

ergetically more favorable to produce from the chlorination of zirconium surfaces.

4. Conclusions

In summary, DFT calculations were carried out to investigate the leading mechanisms and associated energetics of Zr(0001) surface chlorination in gaseous Cl₂ atmosphere. Calculations show that chlorination of Zr(0001) is exothermic by ~3 eV/Cl for dissociative adsorption of a single Cl₂ molecule, and that further chlorination to 1ML and 2 ML under Cl-rich conditions is also exothermic by 1.93 and 2.79 eV/Cl, respectively. Exfoliation of the top Cl–Zr–Cl sandwich layers is among the most energetically favorable degradation pathways leading to Zr(0001) surface dissolution. This can be achieved by Cl atom diffusion into the subsurface, which is hindered by energy barriers of ~3 and ~2.6 eV for diffusion of monatomic Cl through the topmost layer of bare Zr(0001) and 1ML-Cl covered Zr(0001) surfaces. Possible dissociation mechanisms of ZrCl₂, ZrCl₃ and ZrCl₄ molecular species were also assessed using DFT models. Among possible reaction products, formation of ZrCl₄ molecular species is found to be predominant as a result of Zr(0001) chlorination, in agreement with experimental observations.

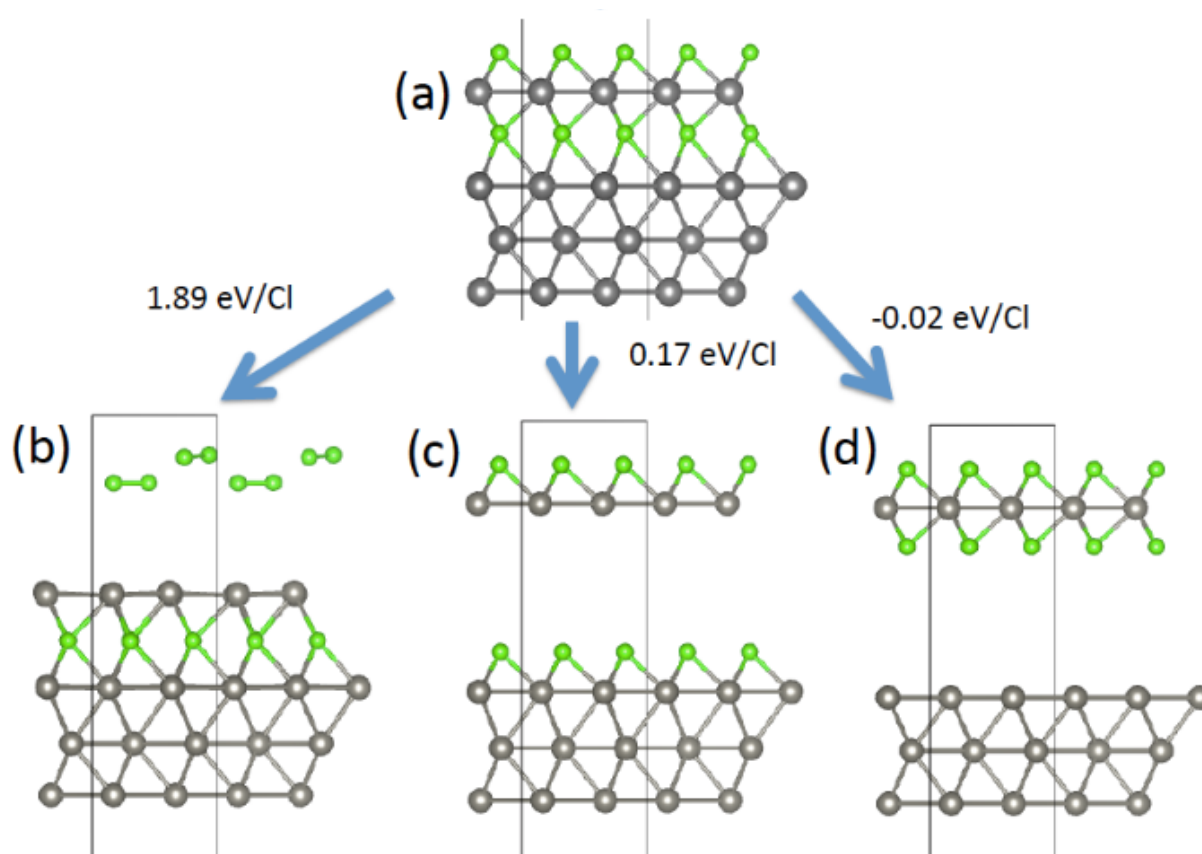
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Graphical abstract



Highlights

- $\text{Cl}_2(g)$ dissociative adsorption on Zr(0001) is exothermic by $\sim 3 \text{ eV/Cl}$.
- Chlorination to 1 and 2 ML under Cl-rich conditions is exothermic by 1.93 and 2.79 eV/Cl.
- Exfoliation of topmost Cl-Zr-Cl sandwich layers is most energetically favorable.
- Formation of ZrCl_4 molecular species upon chlorination is also predominant.