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Chlorine Evolution Reaction on RuO$_2$(110): *Ab initio* Atomistic Thermodynamics Study - Pourbaix Diagrams

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A B S T R A C T

Constrained *ab initio* thermodynamics in the form of a Pourbaix diagram can greatly assist kinetic modeling of a particular electrochemical reaction such as the chlorine evolution reaction (CER) over RuO$_2$(110). Pourbaix diagrams reveal stable surface structures, as a function of pH and the potential. The present DFT study indicates that the Pourbaix diagram in the CER potential region above 1.36 V and pH values around zero is dominated by a stable surface structure in which all coordinatively undercoordinated Ru sites (Ru$_{cus}$) are capped by on-top oxygen (O$_{ot}$). This oxygen saturated RuO$_2$(110) surface is considered to serve as the catalytically active phase in the CER, quite in contrast to the heterogeneously catalyzed HCl oxidation (Deacon process), for which the active RuO$_2$(110) surface is mainly covered by on-top chlorine. The active sites in the CER are suggested to be Ru$_{cus}$O$_{ot}$ surface complexes, while in the Deacon process both undercoordinated surface Ru and oxygen sites must be available for the activation of HCl molecules.

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1. Introduction

One of the greatest challenges in electrocatalysis constitutes disclosing and unraveling the complete reaction mechanism of an electrochemical reaction at the electrode/electrolyte interface and identifying the catalytically active phase or active sites on the electrode surface [1]. From pure macrokinetic experiments (i.e. Tafel slope, reaction order, pH dependence) this ultimate goal cannot be accomplished, but rather this challenging enterprise needs to identify reaction intermediates, which are the most important bit of information to construct the reaction mechanism [2]. In electrocatalysis there are only very few spectroscopic methods available to identify reaction intermediates at the electrode/electrolyte interface, most notable infrared spectroscopy [3,4]. Electron spectroscopy, which has been demonstrated to be pivotal to identify reaction intermediates in heterogeneous catalysis of gas phase reactions [5], cannot be applied due to the presence of the electrolyte solution and the requirement of a sufficiently long mean free path of electrons to reach the detector of the analyzer.

In heterogeneous catalysis of gas phase reactions *ab initio* theory has become a powerful tool [6–8], in particular in combination with surface chemical experiments at single crystalline model catalysts,

in order to aid unraveling the reaction mechanism. However, the full *ab initio* kinetic simulation of a reaction at the catalyst surface is still a demanding enterprise, which needs for instance kinetic Monte Carlo modeling to treat adequately the intricate interplay of the elementary reaction steps at the surface and the exchange of the molecules with the gas phase. Frequently the actual reaction mechanism and the identification of the active surface phase can be decoupled using first principles thermodynamics. *Ab initio* thermodynamics is able to evaluate the stability of a catalyst surface structure under (constrained) reaction conditions as a function of the reaction temperature and reactant pressures by allowing the exposure of the surface to the reactant mixture, but suppressing the actual surface reaction and also a possible solid state transformation of the catalyst (hereafter referred to as "constrained" TD). This active surface phase is then considered a promising starting point of a full kinetic study including surface reactions. For the case of CO oxidation over RuO$_2$(110) this simple approach has succeeded to identify the "active" surface phases under reaction conditions [9], which are compatible with those found by a full (i.e. including the actual reaction) analysis using *ab initio* based kMC simulations [10–12]. For the HCl oxidation reaction (so-called Deacon process) over RuO$_2$(110) Studt *et al.* performed *constrained TD calculations* [13].

In comparison with gas phase reactions in heterogeneous catalysis additional effects such as the solvent and the electrode potential play a predominant role in electrocatalysis so that a full *ab initio* based kinetic modeling of an electrochemical system is

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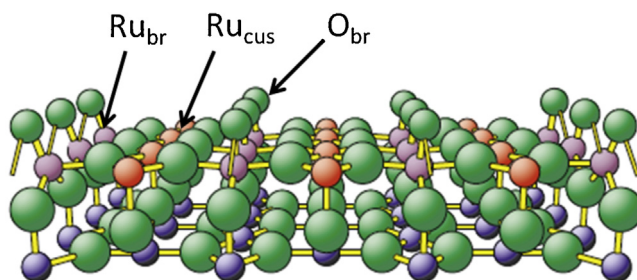Herbert.Over@phys.Chemie.uni-giessen.de (H. Over).

Fig. 1. Stoichiometric RuO$_2$(110) surface. Undercoordinated ruthenium atoms, on which adsorption processes occur, are the 1f-cus ruthenium atoms (denoted as Ru$_{cus}$) and 2f-cus ruthenium atoms (denoted as Ru$_{br}$). Adsorbates in bridge position on Ru$_{br}$ atoms are denoted with the index "br" and adsorbates on Ru$_{cus}$ atoms with the index "ot" (on-top). In case of the stoichiometric RuO$_2$(110) surface the bridge sites are fully covered by bridging oxygen atoms denoted as O$_{br}$. Color code: red balls: ruthenium 1f-cus atoms (Ru$_{cus}$), pink balls: ruthenium 2f-cus atoms (Ru$_{br}$), blue balls: bulk ruthenium atoms, green balls: oxygen atoms.

quite demanding [6,14,15]. Therefore, simple methods are urgently called for in electrochemistry to gain at least some important information of the reaction system, such as the active surface phase of the catalyst under reaction conditions. In electrocatalysis *ab initio* TD can equally be applied to gain important information about the active surface under reaction conditions [16–19]. Here the pH value and the electrostatic potential rather than the partial pressures of the reactants and reaction temperatures are of importance. The resulting (constrained) surface phase diagrams are generally known as (surface) Pourbaix diagrams [20].

In this paper we will concentrate on the chlorine evolution reaction (CER) over RuO$_2$. A detailed comparison of the CER with the related gas phase reaction (Deacon reaction) has recently been presented [21]. In comparison to the oxygen evolution reaction (OER) or the oxygen reduction reaction (ORR) is the CER considered to be much simpler due to the smaller number of transferred electrons (two instead of four electrons) [22]; the CER is almost as "simple" as the prototypical hydrogen evolution reaction in electrocatalysis [23]. Hansen *et al.* [24] had first applied the constrained thermodynamic approach for electrochemistry (EC) to study the reaction mechanism of the CER over RuO$_2$(110) in comparison with that over IrO$_2$(110). In this study solvent effects were neglected which brings Pourbaix diagrams even closer to diagrams of related gas phase HCl oxidation reaction (Deacon process) with the main difference that the energies are references to water in the gas phase instead of stable elements in gas phase. However, a critical comparison with the gas phase HCl oxidation reaction (Deacon process) revealed several open questions [21], which inclined us to thoroughly re-investigate the CER to deepen our understanding of the CER over RuO$_2$(110). In particular, we will be studying the CER within the constraint TD approach, including however solvent effects and addressing the completeness of considered surface structures.

2. Methods

2.1. Calculation Details

All electronic structure calculations have been carried out within the Density Functional Theory (DFT) approach, utilizing the SeqQuest program package [25] and PBE as functional for correlation and exchange [26,27]. The RuO$_2$(110) surface was modeled by a periodic stack of asymmetric slabs containing five O-Ru-O layers with adsorbates only on one side of the slab. Consecutive slabs are separated by a vacuum region of 15 Å. The DFT calculations were restricted to 2 × 1 surface unit cells using a 6 × 6 Monkhorst – Pack **k**-point mesh for slab calculations. In the total energy calculations the atomic geometries of the topmost three layers including the adsorbate layer were optimized, while the atomic positions of the bottom two O-Ru-O layers were fixed. A critical comparison of the

obtained adsorption energies with those derived by VASP calculations [28] indicates that the deviations are within the supposed accuracy of DFT calculations, i.e. less than 0.15 eV per adsorbate.

The 2 × 1 surface unit cell of RuO$_2$(110) contains two bridge (Ru$_{br}$) and two cus sites (Ru$_{cus}$) (cf. Fig. 1). We consider adsorption of O$_{br}$, OH$_{br}$, OCl$_{br}$, and Cl$_{br}$ at bridge sites (Ru$_{br}$) and adsorption of O$_{ot}$, OH$_{ot}$, OCl$_{ot}$, Cl$_{ot}$, Cl(O$_{ot}$)$_2$, (O$_{ot}$)$_2$, (O$_2$)$_{ot}$, and (O$_3$)$_{ot}$, at coordinatively unsaturated sites (Ru$_{cus}$). All possible combinations of adsorption sites and adsorbates were taken into account in this study, giving rise to more than 100 adsorbate structures (cf. supporting information-SI). The adsorption energies of the considered adsorbates are calculated with reference to gaseous chlorine, gaseous hydrogen and water molecules using the chemical potential from water vapor, which is in equilibrium with liquid water at 298 K and 0.035 bar [29].

The changes in the adsorption energy due to the presence of the solvent are estimated by cluster calculations using the Jaguar package [30]. The corresponding cluster model is constructed from 61 atoms and the open valences are saturated by hydrogen. The solvent water is involved implicitly via the self-consistent reaction field (SCRF) approach that describes the solvent as continuum defined by its dielectric constant and the probe radius of the solvent [31]. First, the geometry of the adsorbate structure is optimized for the gas phase, which is associated with an adsorption energy ΔE_{gas}. In a next step, this geometry is fixed and the adsorption energy ΔE_{liq} in presence of water is determined. The solvent effect ΔE_{solv} is then given by:

$$\Delta E_{solv} = \Delta E_{liq} - \Delta E_{gas} \qquad (1)$$

Finally, the total adsorption energy ΔE_{tot} is the sum of the adsorption energy ΔE_{Seq} calculated (for the periodic system) by SeqQuest for the gas phase and the previously determined solvent effect term ΔE_{solv} (see eq. (1)):

$$\Delta E_{tot} = \Delta E_{seq} + \Delta E_{solv} \qquad (2)$$

2.2. Construction of Surface Pourbaix Diagrams

A Pourbaix diagram reveals the thermodynamically most stable structure of the catalyst surface among the set of considered structure as a function of applied electrode potential U and pH [20]. The thermodynamically favoured structure is determined by minimization of the Gibbs enthalpy ΔG among the set of considered surface structures. The Gibbs free enthalpy is given by [24]:

$$\Delta G = \Delta E_{tot} + \Delta E_{ZPE} - T \cdot \Delta S + \Delta G_{ref.} \qquad (3)$$

ΔE_{tot} denotes the adsorption energy in the presence of the solvent (water) calculated by DFT, ΔE_{ZPE} the change in zero-point