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The electrocatalytic properties of doped TiO_2

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ABSTRACT

To rationally control the catalytic properties of heterogeneous catalysts is the goal in heterogeneous (electro)catalysis research. Recent developments of theoretical methods based on density functional theory have enabled computational screening of catalysts, to achieve fundamental understanding of which catalyst is optimal for a certain reaction. In the present work, such screening is employed to elucidate the electrocatalytic properties of doped rutile TiO_2. Electrodes based on this material are widely used in industrial production of, e.g., chlorine and sodium chlorate. The screening covers 38 different dopants, including all fourth, fifth and sixth row transition metals. Several dopants are predicted to activate TiO_2, resulting in a material optimal either for the oxygen evolution reaction, or for selective chlorine evolution. The results can serve as a map for the rational design of electrocatalysts based on TiO_2.

1. Introduction

The efficient production of industrial chemicals requires catalysts that are optimized for the reaction in question. Historically, the optimization of the activity and selectivity of solid catalysts has largely been a question of trial and error, requiring large experimental screening studies. However, the situation has changed during the last few years, with the advent of computational methods to model and predict activities of solid catalysts for any reaction. The steady growth in computational resources now allows for large screening studies, where optimal catalysts for a certain reaction can be predicted [1]. This type of modeling is applicable not only to heterogeneous catalysis, but also to electrochemistry [2,3]. Oxides based on transition-metal doped TiO_2 are important electrocatalysts in electrochemistry. The most important application is in the form of so-called Dimensionally Stable Anodes (DSA), where rutile TiO_2 is doped with Ru, and also other dopants [4]. These electrodes are applied for the industrial production of both chlorine and sodium chlorate [5]. Chlorine gas is one of the fundamental building blocks in industrial chemistry, being produced in amounts exceeding 50-60 million tons every year [5,6], and finding its use mainly in production of PVC and other polymers, but also for water treatment and production of disinfectants and solvents [7]. The pulp and paper industry is the majority consumer of the more than 3 million tons of sodium chlorate produced yearly, where it is used to produce white paper products [8]. The main side reaction in both production of sodium chlorate and chlorine gas is oxygen evolution, which decreases the electrical current efficiency of the production processes by up to around 5% [5,9]. Considering the large yearly production rates of Cl_2 and $NaClO_3$, any increase in current efficiency would have substantial economic value.

RuO_2-TiO_2-based DSA's have been used in industry ever since the 1960s [10,11], and have been devoted both experimental [12–16,4] and theoretical study [17–20]. However, when it comes to other possible dopant materials apart from Ru, experimental studies have mainly focused on the dopants Ir, Sn and Co [21–23]. The relative effects of different dopants on the electrocatalytic properties of the oxide is still unclear, and industrial design of improved DSA's is still governed mainly by trial and error. However, given the industrial and scientific importance of doped TiO_2, a more general fundamental understanding of this group of materials is still required. The theoretical work of García-Mota *et al.* [17,18] was an important first step, where the oxygen evolution reaction (OER) activity of TiO_2 doped with a number of dopants (V, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Ir and Ni) was studied. However, this still leaves out many other possible transition metal dopants, and there are still no broader studies in the literature.

In our previous work [19], we studied the fundamental effects of Ru-doping of TiO_2. The study was based on the descriptor for the chlorine evolution reaction (ClER) and the OER identified by Hansen *et al.* [3] based on density functional theory (DFT)

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calculations. This descriptor is the oxygen adsorption energy, $\Delta E(O^c)$, on the (110) surface of a rutile oxide, and is general for all rutile oxides. Hansen *et al.* [3] also constructed volcano plots for both OER and ClER, determining the descriptor values corresponding to maximum OER activity, and maximum ClER activity and selectivity. Based on calculating this descriptor for OER and ClER for a variety of arrangements of Ru dopants in TiO_2 using DFT, and comparing the descriptor values with the volcano plots, we found [19] that the favorable ClER activity and selectivity of DSA in the original RuO_2-TiO_2 composition is the effect of activation of Ti surface sites by nearby Ru dopants. Thereby, the standard view of DSA [24] as a mixed oxide where the RuO_2 component is associated with activity, and the TiO_2 component is associated with stability and separation of Ru active sites, has to be reconsidered. We also indicated that the approach could be extended to other dopants apart from Ru. Such a screening study would serve as a guide to rational design of TiO_2-based electrocatalysts for both selective chlorine (and sodium chlorate) production, oxygen production, and possibly other reactions that are governed by the same descriptor.

The present work reports the results of such a screening of doped rutile TiO_2. We extend the studies of Karlsson *et al.* [19] to cover a total of 38 dopants (including all third-, fourth and sixth-row transition metals). The study covers the fourth-row elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As and Se, the fifth-row elements Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb and Te and the sixth-row elements Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb and Bi. It complements those of García-Mota *et al.* [17,18]. However, while the studies of García-Mota *et al.* focused only on the OER, the present work puts the results into context of both OER and ClER, and the selectivity between those reactions. As the correct description of mixed oxide systems is believed to be a weakness of common generalized gradient approximation (GGA) exchange-correlation (XC) functionals, due to incomplete correction for self-interaction errors (SIE), the accuracy of our calculated adsorption energies will be discussed based on Hubbard-*U* corrected GGA calculations [25] performed for the doped systems. Then, the results of the screening based on the electrocatalytic properties of the dopants when occupying the active site, and their ability to activate nearby Ti sites, are discussed. Thereby, a complete fundamental picture of the electrocatalytic properties of doped TiO_2 is given. The calculated descriptor values can be used, together with the volcano plot of Hansen *et al.* [3], to choose dopants based on the reaction for which the TiO_2 material is to be optimized. We find that the ability to activate Ti surface sites is not unique to Ru. In fact, several other transition metals have this same ability. Still, the ability is not universal, and several transition metals have little effect on, or even result in a further decrease in, the activity of Ti. We also study the effect of combining different dopants to activate the same Ti site, finding that this approach can be used to control the activity beyond the possibilities in binary Ti-based oxides. Furthermore, the driving force for movement of a dopant in the mixed oxide is considered based on energy differences between different arrangements of a dopant in the host TiO_2 structure, giving a first understanding of which sites the dopant is more likely to occupy. We find that during OER, a driving force exists to move certain dopants toward the surface, and that this driving force might help explain the deactivation of industrial DSA. Then, we perform a more detailed study of charge transfer between dopant and the host oxide in Ru-doped TiO_2, based on Bader charges [26]. This part attempts to give a more fundamental explanation for the activation of Ti, based on the Ru dopant as a prototype case. Both the previous [19] and the present study are based on the calculation of the descriptor value found by Hansen *et al.* [3]. Recently, Bendtsen *et al.* [27] suggested that doping RuO_2 with Co or Ni opens up a new pathway for OER than has been considered previously, and we will also consider this suggestion in the context of doped TiO_2 in the final part of the paper.

2. Computational methods

Most computational settings were the same as in the previous study by Karlsson *et al.* [19]. All DFT calculations were performed using GPAW [28] and the GPAW atomic projector augmented wave (PAW) setups version 0.9.9672. The RPBE [29] GGA XC functional was used in all calculations. As in the previous study [19], the adsorption energy of oxygen on the coordinatively unsaturated site (cus), O^c, is calculated with H_2 and H_2O in vacuum as reference states [3]:

$$\Delta E(O^c) = E\left(O^c\right) - E\left(^c\right) - E(H_2O) + E\left(H_2\right), \tag{1}$$

where $E\left(O^c\right)$ is the energy of a surface with a relaxed O^c adsorbate and $E(^c)$ is the energy of a surface without the same adsorbate. The adsorption calculations were performed either in the GPAW finite-difference mode, using a grid spacing of 0.18 Å, or in the GPAW plane-wave (PW) mode, using a PW cutoff of 500 eV. All model systems used in the calculations consisted of perfect 4-layer rutile metal oxide slabs, the same number of layers as in the studies of Hansen *et al.* [3] and Karlsson *et al.* [19]. Defects were thus not considered, but we note that defective surfaces in general bind adsorbates more strongly [30], and that this then likely results in too-strong adsorbate-surface binding to achieve an active and selective ClER electrocatalyst [3,19]. All calculations were fully periodic. As in the previous study [19], the dipole correction [31] was not included in the dopant screening calculations. The effect of including the dipole correction on O adsorption energies on TiO_2, RuO_2 and Ru-doped TiO_2 was found to be less than 5 meV in that previous study. However, the dipole correction was applied for the calculations in Section 3.6, where we discuss the alternative OER mechanism of Bendtsen *et al.* [27]. Each slab was separated from the next slab in the *z* direction by 16 Å of vacuum.

The periodic oxide model systems used for screening calculations consisted of a unit cell with a 1x1 surface with 2 surface sites (one bridge site and one cus site, see Fig. 1). This means that the calculations correspond to the case of 100% surface adsorbate coverage. Effects of lower surface coverages will thus not be considered. Increased adsorption energies can be expected at lower

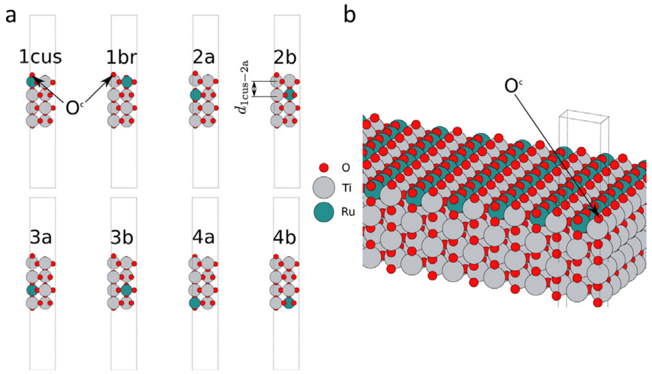

Fig. 1. Graphical representations of the dopant arrangements and systems considered in the present work, using the case of Ru as dopant as an example. a) Side-view of the slab considered, with the different cation positions indicated. The O^c adsorbate is highlighted for just the 1cus and 1br cases, but is found in the same locations in all other systems as well. The distance parameter $d_{1cus-2a}$, the distance between the 1cus and 2a sites, is indicated for the example of system "2b" (where the Ru dopant occupies the 2b site). Dashed lines indicate the unit cell. The *z* axis is vertical in the image, the *x*-axis is horizontal and the *y*-axis is directed into the plane. b) The optimized structure of O^c adsorption on a 1x1 slab of Ru-doped TiO_2. The Ru dopant is seen forming the surface layer bridge site. This system is the "1br" case. The unit cell used in the calculations is indicated by the dashed lines. The unit cell is repeated several times in the *x* and *y* directions to clarify the structure of the slab. The *x* direction is oriented from bridge site to bridge site across the cus sites, while the *y* direction is oriented along the lines of bridge (or cus) sites. The *z* direction is normal to the surface.