Theoretical study of proton binding behavior at the rutile (001) (1x1) crystal face

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The quantum chemistry methods are employed to study the singly coordinated surface oxygens on the rutile unreconstructed (001) crystal face. The ab-initio predicted charges and proton affinity constants are combined with the Grand Canonical Monte Carlo simulations of the proton binding in order to obtain H+ ions adsorption isotherms. The experimental study of this crystal face is impossible due to its instability, but the same surface sites can be find on the most stable (110) surface. In both quantum chemistry calculations and simulations the solvent is included by using the reaction field approach. In the ab-initio calculations it was achieved by employing the COSMO-RS model while in the simulation procedure by using the Borkovec [1] interaction potential (which includes the polarization effects). The theoretical predictions are very close to the experimental ones, even if the size of the clusters is relatively small.

1. INTRODUCTION

Metal (hydro)oxides possess the charged surface sites due to non-saturated charges on the surface oxygens. The primary surface charge is determined by the proton binding reactions, and this process is treated as initial in creating the double electrical layer at the metal oxide/electrolyte interface. Proton binding is frequently described by using the SCM (Surface Charging Mechanism) models [2]. There are a few commonly used models: 1-pK [3], 2-pK [4], MUSCI [5] and CD-MUSIC [6]. Generally, they differ in a number of the proton binding reactions and the assumed charge on the surface empty site.
On such charged surface sites the adsorption of oppositely charged ions take place. Hence, hydrogen ions play the role of potential determining ions for metal oxides, the number of ions bound to the surface (fractional coverage) changes according to pH of the bulk phase.

Proton affinity for metal oxides as well as charges of the surface groups (predicted by SCM models) are of special interest because they describe the acid-base properties of the metal oxides quantitatively [7]. The most frequently obtained quantity is the point of zero charge, i.e. a certain pH value at which the surface is uncharged. If there is no specific adsorption pzc is the same as the pristine point of zero charge (ppzc) and in this case pzc is equal to the equilibrium constant of the proton binding reaction (or algebraic average of equilibrium constants if proton binding is described by more than one reaction) [2].

There are a few metal oxides of special interest (silica, aluminum oxide, titanium oxide), mostly because of their widespread practical applications. In this study we focus our attention on titanium dioxide.

Titanium dioxide is oxide of titanium naturally occurring, occurring oxide of titanium, which occurs in a few polymorphic forms [8,9], for example (occurring at atmospheric pressure): rutile, anatase, brookite TiO$_2$ (B). Rutile is the thermodynamically stable polymorphic form of TiO$_2$ at room temperature, its crystal structure is a member of C4 crystal group (space group is P4$_{2}$/mnm or in the Person nomenclature tP6) [8,9]. The elementary unit consists of two titanium atoms and four oxygen atoms. The dimensions of the elementary cell are [9]: a = 4.593 Å and b = 2.956 Å. Many other metal oxides crystallize in the rutile crystal type, for example: PbO$_2$, CoO$_2$, NbO$_2$, MoO$_2$, SnO$_2$, WO$_2$, MnO$_2$, RuO$_2$. The only difference between the structure of TiO$_2$ and other oxides which crystallize in C4 type is the length of the translation vectors. The dominant faces of rutile are (110) and (100) [8,9], and they are the most frequently studied. In this study we focused our attention on the (001) crystal face, which has not been studied so far. It is well known that (001) crystal face occurs mostly in reconstructed or relaxed state. For these reasons, it is extremely difficult to perform experiments on this crystal face.

According to the research by Bourikas et al. [10] the acid-base properties for the crystal faces (001), (010) and (100) are very similar. Due to the fact that MUSIC estimations were published only for stable crystal faces crystal face, we compared the ab-initio predictions of the (001) surface with those for stable one published by Hiemstra et al. [11].

The pzc value of the various ideal crystal planes is identical [10]. Moreover, they have proved that its value is very close for both singly (TiO$^{1/3}$) and doubly (Ti$_2$O$^{2/3}$) coordinated surface oxygens. There are several pzc values for rutile in literature, most of the results are around 6.0.
Fig. 1. Rutile (001) crystal face. Part A – the bulk crystal phase, B – one layer of elementary unit cell, C – the derivation of the surface periodic element from the elementary unit, D – the surface sites with the OH group and OH$_2$ groups (proton binding process).
If there is no specific adsorption $pK_H$ is equal to $pzc$ (if $K_H$ is the equilibrium constant for desorption process). $pzc$ of TiO$_2$ is usually determined by means of the potentiometric titration technique, in which the dispersions of oxides can be only used. According to Kosmulski [12] the recommended value for both anatase and rutile is 5.9, however, it is an average value whose applicability is limited to the macroscopic studies. In reality the surface site density and $pzc$ value depend on the crystal face. According to Hiemstra et al. [11] for the 100 crystal face $N_s$ equals 7.4 sites/nm$^2$ and the proton affinity constant ($pK_H$) equals 7.5.

Recently, Predota et al [13,14] have published very interesting MD studies of ions adsorption on the rutile (110) crystal face. The continuation of this research is the paper of Zhng et. al [15], in which the precise MD study of many crystal faces was compared with the X-ray measurements. An example of using ab-initio molecular dynamics method was presented by Kornherr et al. [16] and by Jog et al [17]. There are also many strictly ab-initio studies of rutile surface, for example paper of Muscat et al. [18].

In our previous paper [19] we employed the similar procedure for the amorphous aluminum oxide surface. For the aluminum oxide the calculations were not as expensive as for the titanium one (four raw elements), but the amorphicity of the surface results in the necessity of building appropriate clusters. In the case of TiO$_2$, the initial geometry can be derived from the crystallographic data.

This paper is an example of the molecular approach to the periodic systems, that is, it employs the classical quantum chemistry machinery (based on the molecular orbitals) [15]. From the physical point of view, the more correct approach is based on the Crystal Orbitals (CO), but the molecular approach can be carried out by using almost any kind of the computational package, and as a result it is more popular. The details of the presented ab-initio calculations as well as for the computer simulation procedures can be found in our previous papers [19,21,22]. The quantum chemistry calculations were carried out by using PQS package [23].

2. THEORY

The protonation reaction for a singly coordinated surface oxygen can be written as follows:

$$\equiv TiOH^{0+1} + H_2^0 \rightarrow ^\text{H} TiOH^0 + H_2O^+$$

(1)

where $Q$ is the charge of an empty surface site. This surface process is schematically presented in Figure 2.
According to the MUSIC model [11], charge of this group (Q) can be estimated by using Pauling's concept of the local neutralization of the charge. Application of the MUSIC model to titanium dioxide results in the estimation that $Q = -\frac{1}{3}$ [11].

Next, the energy of dissociation $\Delta E_H$ can be calculated from ab-initio results. It is well known that this reaction is exothermic [24], this means that $\Delta E_H$ has to be positive. In calculation of this energy the correction for basis set superposition error (BSSE) [25] has to be included. It is usually achieved by employing the Counter Poise correction [25]. If we assume that the surface reaction is carried out under the constant pressure (isobaric) and the entropy changes may be neglected (isoentropic) the free energy is equal to the inner energy. It is undoubtedly true, that surface complexation is not a isoentropic process, but the entropic changes cannot be observed if the solvent molecules are not included explicitly. Finally, we can estimate the $pK_H$ value by employing the formula:

$$pK_H = A \frac{n \Delta G_H^o}{RT}$$  \hspace{1cm} (3)$$

where $n = 1/\ln(10)$, $R$ is a gas constant, $T$ is temperature (293K). A similar approach was presented by Klamt [26], and by us in our previous paper [19]. The value $A$ is a so-called scaling factor, which guarantees that the estimated $pK_H$ value belongs to the period (0;14).

The ab-initio calculations consist of two stages: the first one is calculation of the energy by the DFT approach, and the second one is a partitioning of the functional (Hermit) space between atoms in the cluster. The DFT calculations are carried out by using B3LYP potential for the Pople style basis set (6-31G) and by using BVP86 potential for the Ahlrichs' valance split basis sets. The results for different basis sets with polarization functions as well as for different
exchange-correlation potentials will be presented later. As it was mentioned in
the second stage, the functional quantum population analysis (QPA) is
performed. Generally speaking, the population analysis can be divided into three
groups: partitioning of the real space (e.g. Barder analysis of electron density
based on the Atoms in Molecule concept), partitioning of the functional space
(Mulliken and Löwdin for the basis set and Weinhold NPA – Natural Population
Analysis for Natural Bond Orbitals) and the third group – fitting the charges to
reproduce the electrostatic potential (e.g. Merz-Singh-Kollman scheme). In this
paper the discussion is limited to the partitioning of the Hermit (functional)
space. As it was mentioned, the calculations are not carried out for the basis sets
with the polarization functions. It is due to the fact that the pure \( f \)-functions have
not been supported by NBO 5.0 package \[27\] so far, so at present, the Weinhold
analysis cannot be performed for such basis sets.

The presence of the solvent is introduced into the quantum chemistry
calculations by using SCRF (Self-Consistent Reaction Field) models, also known
as Continuum Solvent Models \[28\]. All SCRF models have in common creation
of the cavity around the solute molecule, outside the cavity the solvent is
represented by the continuum uniform polarizable medium with the dielectric
constant of \( \varepsilon \). One of such SCRF models was introduced by Klamt \[29\] and is
known as COSMO-RS (Conductor Like Screening Model for Real Solvent). In
COSMO \( \varepsilon \) changes from the specific value to the infinity, in the currently used
modification COSMO-RS describes the interactions in a fluid as local contact
interactions of molecular spheres. For each solvent and solute (i.e. for each atom
of the solute molecule), Klamt \[29\] employed the fitting procedure to estimate
the appropriate COSMO-RS parameters.

It is worth mentioning here that the ab-initio estimated pK\(_{\text{H}}\) value is the
macroscopic one, i.e. it can be compared with the experimentally determined
pzc. If we want to keep the constant pzc for different input charges (obtained
from the QPA analysis) we have to recalculate pK\(_{\text{H}}\) by subtracting the lateral
interactions contribution. For this reason, we employed the MFA approach. In
Table 2 the simulation results are listed, the details of the MFA approach and its
usage in order to recalculate ab-initio pzc were published elsewhere \[19\].

3. RESULTS

Some of the macroscopic parameters are set up to the literature values.
According to Bourikas et al. \[12\], the dielectric constant near the rutile surface
equals 40, while in the bulk phase we assumed \( \varepsilon=78 \) (the same as in COSMO-
RS). The surface site density for (100) crystal face of rutile is equal to
7.4 sites/nm\(^2\) according to the above mentioned paper of Bourikas et al. \[12\].
Due to the lack of data for (001) surface we used instead the data for (100). To obtain such surface site density mentioned above, we assume that the surface space is d=0.368 nm. In this paper we simplify the surface model, assuming that simulation can be carried out on the regular cubic (1x1) lattice with an appropriate vector of translation (d). In next step, we prepare a more realistic model of rutile surface, i.e. derived from the atomistic picture of the surface. Similarly, to our previous papers [19,21-22], we employed Borkovec potential [1], which contains the solvent polarization effects (ε=78, ε_s=40, 1/κ =0.43 nm, a = 0.1 nm, T=293 K, meaning of these parameters is explained in papers [19,21,22]). The simulations are carried out for the homogeneous surface, i.e. the identical microscopic pK_H value is associated with each surface site.

Tab. 1. Results of DFT calculations for the rutile surface (M – Mulliken, L – Löwdin, W – Weinhold (NPA) analysis). The experimental pK_H value for (100) crystal face of rutile is equal to 7.5 [12].

<table>
<thead>
<tr>
<th>Theory level</th>
<th>ΔE_Ti</th>
<th>BSSE</th>
<th>ΔE_W</th>
<th>BSSE</th>
<th>pK_H</th>
<th>Charge</th>
<th>QPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G</td>
<td>1851.041</td>
<td>-1.472</td>
<td>-1098.633</td>
<td>-16.606</td>
<td>7.6084</td>
<td>-0.744598</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
<tr>
<td>BVP86/svp-Ahlrichs</td>
<td>1851.805</td>
<td>-11.985</td>
<td>-1098.633</td>
<td>--16.602</td>
<td>7.47508</td>
<td>-0.466501</td>
<td>M</td>
</tr>
<tr>
<td></td>
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<tr>
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<td>-1057.511</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
</tr>
</tbody>
</table>

In Table 1 the results of ab-initio calculations are collected, while in Table 2 the simulation parameters are derived from Table 1 by employing the MFA approach.

In Figure 1 the way in which the computational cluster was obtained is presented. The appropriate fragment of the elementary unit is chosen, and reoriented according to direction of the (001) plane. The chosen fragment of the molecule (Fig. 1C) has the fixed positions of all atoms (according to the crystallographic data). In order to study proton binding, we add OH group and reoptimize its position (B3LYP/6-31G) by keeping fixed the remaining cluster.
The cluster after adsorption was obtained from (TiOH) by adding another hydrogen atom to surface oxygen and by reoptimizing the surface group again.

Tab. 2 Simulation parameters obtained from the DFT results by using MFA the approach \((\varepsilon=78, \varepsilon_s=40, 1/\kappa=0.43\ \text{nm}, a=0.1\ \text{nm}, T=293\ \text{K})\).

<table>
<thead>
<tr>
<th>Charge</th>
<th>QPA</th>
<th>(pK_{H_{\text{macro}}n}^{m} )</th>
<th>interactions parametr (\mathcal{C})</th>
<th>(pK_{H_{\text{macro}}n}^{m}=pzc + \frac{1}{\mathcal{C}}n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.744598</td>
<td>M</td>
<td>7.60804</td>
<td>4.3743</td>
<td>8.55791</td>
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<td>-0.300996</td>
<td>L</td>
<td>7.60804</td>
<td>32.7657</td>
<td>14.723</td>
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<td>-0.44298</td>
<td>W</td>
<td>7.60804</td>
<td>20.8066</td>
<td>12.1261</td>
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<tr>
<td>-0.466501</td>
<td>M</td>
<td>7.60804</td>
<td>19.0865</td>
<td>11.6197</td>
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<tr>
<td>-0.135099</td>
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<td>7.60804</td>
<td>50.164</td>
<td>18.3681</td>
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<td>W</td>
<td>7.60804</td>
<td>28.2246</td>
<td>13.604</td>
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<tr>
<td>-0.658081</td>
<td>M</td>
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<td>7.83982</td>
<td>9.31044</td>
</tr>
<tr>
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<td>39.2379</td>
<td>16.1284</td>
</tr>
<tr>
<td>-0.33910</td>
<td>W</td>
<td>7.60804</td>
<td>29.2908</td>
<td>13.9685</td>
</tr>
</tbody>
</table>

Fig. 3. Adsorption isotherms for charges obtained from QPA at different theory level.
Reoptimalization of the surface group after adsorption represents the dynamic relaxation of the adlayers, which takes place in reality.

In Figures 3 and 4 the simulation results are presented. As it was mentioned all isotherms have a intersection point at $\phi=0.5$ (inflection point), which is tantamount to saying that all surface charge density curves have the same pzc value (Figure 4). This condition was obtained by recalculation of ab-initio pK$_H$ using the MFA approach. The behavior of the isotherms is easy to predict, the higher negative QPA charge the smaller lateral interactions between the adsorbed ions and finally higher fractional coverage for a given pH value. The results presented in this paper are quite different from our previous ones, due to the totally different interaction parameters and surface site density.

Fig. 4. Surface charge density curves for charges obtained from Weinhold (NPA) analysis, for various theory level. The curves $\sigma_0=f(pH)$ intersect the line $\sigma_0=0$ at different pH values (pzc-points).

4. CONCLUSIONS

At present, in many studies the ab-initio methods are combined with the statistical ones. This cooperation gives more profound understanding of the process in question. The classical computer simulation methods require many assumptions in description of the molecular level of the system, most of them
can be obtained from the ab-initio studies or other independent spectroscopic or
crystallographic experiments. At the moment, the most promising method is the
ab-initio molecular dynamics (Car-Parrinello method), unfortunately, it is too
expensive (for the current day computers) to be employed in many molecule
systems (e.g. in studying of adsorption from liquid phase), for this reason the
simplified approach is presented here. The adsorption energy and surface
charges are derived from the quantum chemistry calculations, the potential
parameters are set up to literature suggestions. The estimated pzc from the ab-
initio calculations is very close to the experimental ones (even if we compared
them for a slightly different crystal face), and the charges are close to the
MUSIC predictions (-1/3). Moreover, the Monte Carlo simulation results give
acceptable results, and we support the MUSIC model, as the only one in this
case. Contrary to the real experiment, we can carry out the computer
potentiometric titration on a one monocrystal face. The experiment of
potentiometric titration gives always the surface charge density for the
suspension, which even if obtained from the monocrystal possesses particles
exhibiting many crystal faces. This is evidently the advantage of computer
simulation methods over the experimental ones. The presented primary results
courage to study all crystal faces (including various coordination) on all
titanium dioxide forms.

In this paper we confined our interest only to unstable (001) crystal face of
rutile. In literature we can find a lot of computer simulation results, but none of
them presents predictions for pzc and verification of SCM. The complete study
of titanium dioxide is under preparation, and will be published soon.

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CURRICULUM VITAE

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