ELECTROSTATIC POTENTIAL CALCULATIONS ON CRYSTALLINE TiO₂: THE SURFACE REDUCIBILITY OF RUTILE AND ANATASE

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From calculations of the electrostatic potential at the most densely packed rutile (110) and anatase (001) crystal faces, greater reducibility of the coordinatively unsaturated Ti⁴⁺ ions at the rutile surface than at the anatase surface is predicted. Consequently, the intrinsic Lewis acidity of coordinatively unsaturated Ti⁴⁺ ions at the (110) face of rutile is larger than that of the Ti⁴⁺ ions at the anatase face. This may relate to some experimentally observed differences in catalytic activity between rutile and anatase.

1. Introduction

In the following sections we present the results of

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electrostatic potential calculations on rutile and anatase. Rutile and anatase are both crystal modifications of TiO₂, which show markedly different catalytic activities in chemical reactions. Several examples of this phenomenon have been reported in the literature [1–3].

Table 1
Crystallographic data and bulk chemical properties of rutile and anatase

	Rutile	Anatase
space group a)	P4 ₂ /mm (D _{4h})	142m (D _{2d})
packing mode a)	hexagonal	cubic
<i>a</i> (nm) a)	0.459375	0.3785
<i>c</i> (nm) a)	0.295812	0.9514
<i>u</i> a)	0.3053	0.2066
coordination number Ti ⁴⁺	6	6
coordination number O ²⁻	3	3
Ti–O bond lengths (nm) b)	0.1946 ₁ 0.1983 ₄	0.1937 ₀ 0.1965 ₆
lattice energy (kJ mol ⁻¹) c)	–13623	–13669
Δ <i>H</i> _{f, 298.15 K} ⁰ (kJ mol ⁻¹) d)	–943.5	–912.5
Δ <i>S</i> _{298.15 K} ⁰ (J mol ⁻¹ K ⁻¹) d)	49.92	50.25
density (g ml ⁻¹) d)	4.27	3.90

a) Ref. [4]. b) Calculated using Wyckoff's [4] data. c) See ref. [5]. d) Ref. [6].

Fig. 1. Structure of the rutile (110) face. At the surface ($l = 0$) five- (type I, C_{4v}) and six-coordinated (type II, D_{4h}) Ti^{4+} ions are present. Surface O^{2-} ions appear in two- (type IV) and in three-coordinated (type III, V) environment. $\bullet = Ti$, $\circ = O$, $\square =$ surface oxygen vacancy.

In the reaction referred to rutile is a far more active catalyst than anatase. This seems at first sight rather surprising, since the crystallographic data and bulk chemical properties (see table 1) of rutile and anatase

are very similar. However, differences occur in the second and higher coordination shells of Ti. It is the purpose of this letter to show how this affects the surface electrostatic potentials of the most densely packed

Fig. 2. Structure of the anatase (001) face. At the surface ($l = 0$) both two- (type II) and three-coordinated (type I) O^{2-} ions are present. Surface Ti^{4+} ions appear exclusively in five-coordinated (D_{2d}) environment. $\bullet = Ti$, $\circ = O$, $\square =$ surface oxygen vacancy.

Fig. 3. Structure of the rutile (001) face. At the surface ($l = 0$) Ti^{4+} is exclusively four coordinated (C_{2v}) and O^{2-} is exclusively two coordinated. $\bullet = \text{Ti}$, $\circ = \text{O}$, $\square =$ surface oxygen vacancy.

faces of anatase and rutile and hence the Lewis acidity of the cations or basicity of surface anions. The calculations predict that one may expect a distinct difference in reducibility of the Ti^{4+} ions at these surfaces.

Calculations have been carried out on the stable, most densely packed rutile (110) and anatase (001) faces and on the stable rutile (001) face.

At the rutile (110) surface both five- and six-coordinated Ti^{4+} are present (fig. 1). At the anatase (001) surface Ti^{4+} is five coordinated (fig. 2) and at the rutile (001) surface Ti^{4+} is four coordinated by oxygen ions (fig. 3).

2. Calculation procedure

For the calculation of the electrostatic potential several methods have been developed [7–10]. For our calculations we selected the method originally devised by Evjen [8] for bulk potential calculations. Unlike the other methods, the Evjen method allows simple programming, and, what is most important is easily modified to facilitate potential calculations in semi-infinite crystals. Madelung constants $M(r_0)$ were calculated according to the definition:

$$U = \frac{1}{2n} \sum_k q_k e \sum_l' \sum_j q_j e / |r_l + r_j - r_k|$$

$$= \frac{1}{2n} \sum_k q_k e \phi_k(r_k) = -M(r_0)(ze)^2/r_0, \quad (1)$$

in which U is the electrostatic lattice energy; n is the number of molecules in the unit cell; $\phi_k(r_k)$ is the electrostatic potential of ion k , at position r_k and with charge $q_k e$, generated by all other ions (characterized by position vectors $r_l + r_j \neq r_k$ and charges $q_j e$) in the lattice; k runs over the ions making up the unit cell; r_0 is the nearest-neighbouring distance, and z is the largest common factor of the q_k . For a TiO_2 lattice, eq. (1) reduces to:

$$M(r_0) = (r_0/2e)[\phi(\text{Ti}^{4+}) - \phi(\text{O}^{2-})]. \quad (2)$$

As far as the quantities $M(r_0)$ and also E_T [see eq. (5)] are concerned, the calculated results are very accurate; the accuracy solely being determined by the accuracy of the input data (≥ 4 significant digits in all cases). The calculated electrostatic potentials ϕ , however, are considerably less accurate (estimated absolute accuracy ≈ 0.05).

3. Results and discussion

The results of our electrostatic potential calculations are given in tables 2, 3 and 4 for the rutile (001), the rutile (110) and the anatase (001) faces, respectively. A comparison of the Madelung constants $M(r_0)$ as a function of the layer number $l^\ddagger$ shows that it behaves roughly in the same way for the rutile (001) and the

‡ l counts the number of layers, starting from the surface ($l = 0$). See also figs. 1, 2 and 3.

Table 2

Electrostatic potentials $\phi(\text{Ti}^{4+})$ and $\phi(\text{O}^{2-})$ and Madelung constants $M(r_0)$ ($r_0 = 0.1946_1$ nm) as a function of the layer number l , for the rutile (001) face

l	$\phi(\text{Ti}^{4+})$ ($e \text{ nm}^{-1}$)	$\phi(\text{O}^{2-})$ ($e \text{ nm}^{-1}$)	$M(r_0)$
		2.3 ₄ a)	
0	-27.3 ₈ b)	15.4 ₁ b)	4.1632 ₅ b)
1	-31.9 ₉	18.1 ₆	4.8802 ₂
2	-31.2 ₁	17.8 ₁	4.7594 ₆
3	-31.2 ₁	17.8 ₄	4.7735 ₃
4	-31.2 ₂	17.8 ₂	4.7716 ₂
5	-31.2 ₃	17.8 ₁	4.7718 ₇
6	-31.2 ₄	17.8 ₀	4.7718 ₄
7	-31.2 ₅	17.7 ₉	4.7718 ₄
8	-31.2 ₆ c)	17.7 ₈ c)	4.7718 ₄ c)

a) Electrostatic potential $\phi(v)$ at the surface oxygen vacancy.

b) Surface value. c) Bulk value.

Table 3

Electrostatic potentials $\phi(\text{Ti}^{4+})$ and $\phi(\text{O}^{2-})$ and Madelung constants $M(r_0)$ ($r_0 = 0.1946_1$ nm) as a function of the layer number l , for the rutile (110) face

l	$\phi^{(5)}(\text{Ti}^{4+})$ a) ($e \text{ nm}^{-1}$)	$\phi^{(6)}(\text{Ti}^{4+})$ b) ($e \text{ nm}^{-1}$)	$\phi^{(3)}(\text{O}^{2-})$ c) ($e \text{ nm}^{-1}$)	$M(r_0)^{(5)}$ a)	$M(r_0)^{(6)}$ b)
			7.9 d)		
0	-20.5 ₃ e)	-24.1 ₆ e)	26.8 ₇ e)	4.6131 ₃ e)	4.9664 ₂ e)
1	-22.6 ₈	-22.5 ₃	26.4 ₁	4.7764 ₉	4.7623 ₁
2	-22.6 ₄	-22.6 ₇	26.4 ₀	4.7716 ₃	4.7752 ₄
3	-22.6 ₇	-22.6 ₇	26.3 ₆	4.7718 ₅	4.7718 ₂
4	-22.7 ₀	-22.7 ₁	26.3 ₃	4.7718 ₄	4.7718 ₄
5	-22.7 ₄ f)	-22.7 ₄ f)	26.3 ₀ f)	4.7718 ₄ f)	4.7718 ₄ f)

a) See fig. 1, type I. b) See fig. 1, type II. c) See fig. 1, type III.

d) Electrostatic potential $\phi(v)$ at the surface oxygen vacancy. e) Surface value. f) Bulk value.

Table 4

Electrostatic potentials $\phi(\text{Ti}^{4+})$ and $\phi(\text{O}^{2-})$ and Madelung constants $M(r_0)$ ($r_0 = 0.1937_1$ nm) as a function of the layer number l , for the anatase (001) face

l	$\phi(\text{Ti}^{4+})$ ($e \text{ nm}^{-1}$)	$\phi^{(2)}(\text{O}^{2-})$ a) ($e \text{ nm}^{-1}$)	$\phi^{(3)}(\text{O}^{2-})$ b) ($e \text{ nm}^{-1}$)	$M(r_0)^{(2)}$ a)	$M(r_0)^{(3)}$ b)
		2.3 ₀ c)			
0	-28.6 ₆ d)	17.2 ₉ d)	19.9 ₂ d)	4.4505 ₃ d)	4.7052 ₀ d)
1	-29.5 ₆	19.6 ₆	19.6 ₃	4.7664 ₆	4.7633 ₅
2	-29.5 ₇	19.6 ₃	19.6 ₃	4.7653 ₉	4.7653 ₂
3	-29.5 ₉	19.6 ₁	19.6 ₁	4.7653 ₁	4.7653 ₁
4	-29.5 ₉	19.6 ₁	19.6 ₁	4.7653 ₁	4.7653 ₁
5	-29.5 ₈	19.6 ₃	19.6 ₃	4.7653 ₁	4.7653 ₁
6	-29.5 ₈ e)	19.6 ₂ e)	19.6 ₃ e)	4.7653 ₁ e)	4.7653 ₁ e)

a) See fig. 2, type II. b) See fig. 2, type I.

c) Electrostatic potential $\phi(v)$ at the surface oxygen vacancy.

d) Surface value. e) Bulk value.

rutile (110) face. In both cases $M(r_0)$ exhibits a minimum at the surface ($l = 0$), a maximum at the layer immediately below the surface ($l = 1$) and converges to an intermediate bulk value of 4.7718₄. The minimum at the surface is of course due to coordinative unsaturation. The fact that in the case of rutile the (110) surface ($M(r_0) = 4.6131_3$) is electrostatically more stable than the (001) surface ($M(r_0) = 4.1632_5$) reflects the larger degree of coordinative saturation and the denser packing of the ions at the (110) surface.

The maximum value of $M(r_0)$ at the layer immediately below the surface ($l = 1$) is inherent in the hexagonal structure of rutile. It is explained by the fact that the layer immediately below the surface ($l = 1$) suffers significant repulsion from only one neighbouring layer ($l = 3$), while deeper layers ($l = i, i > 2$) suffer significant repulsion from two neighbouring

Table 5

A comparison of the Madelung constants $M(r_0)$ calculated from Watson's data [5], with our results, for the rutile (001) face

l	Madelung constant $M(r_0)$	
	Watson's work	our work
0	4.162 ₃	4.1632 ₅
1	4.881 ₁	4.8802 ₂
2	4.760 ₈	4.7594 ₆
3	4.774 ₆	4.7735 ₃
4	4.772 ₇	4.7716 ₂

layers characterized by $l = i - 2$ and $l = i + 2$ respectively. The layers in cubic structures like anatase do not suffer significant repulsion from any neighbouring layers, and therefore the relation between $M(r_0)$ and l does not show a maximum at $l = 1$. The calculated bulk Madelung constants for both rutile ($M(r_0) = 4.7718_4$) and anatase ($M(r_0) = 4.7653_1$) are in excellent agreement with the results of van Gool [11] ($M(r_0) = 4.772_0$ for rutile, $M(r_0) = 4.765_1$ for anatase, Ewald method). Very recently, Watson [5] calculated the difference between the electrostatic potentials at the l th layer and the bulk as a function of l , for the rutile (001) face. Transformation of these potential differences into Madelung constants reveals a satisfactory agreement with our results, as can be seen from table 5. The slight deviations occurring in table 5 can be attributed to the fact that Watson used slightly different unit cell parameters for rutile in his calculation.

In the preceding paragraphs we have seen that for

both the (110) and the (001) face of rutile, the Madelung constant $M(r_0)$ converges to a common bulk value at large l . This is not true, however, for the potentials $\phi(\text{Ti}^{4+})$ and $\phi(\text{O}^{2-})$ of the Ti^{4+} and O^{2-} ions. From tables 3 and 4 it can be seen that these differ by a factor:

$$\begin{aligned} \Delta\phi &= \phi(\text{Ti}^{4+})(110) - \phi(\text{Ti}^{4+})(001) \\ &= \phi(\text{O}^{2-})(110) - \phi(\text{O}^{2-})(001), \end{aligned} \quad (3)$$

which converges to a constant value of 8.52 e nm^{-1} for the bulk electrostatic potentials. This implies that either the rutile (001) or the rutile (110) should have a finite dipole moment. From the surface structures (figs. 1 and 3) it is evident that the rutile (110) surface exhibits a dipole moment, perpendicular to the surface.

According to electrostatic theory, $\Delta\phi$, when evaluated for the limiting case of the bulk electrostatic potentials, is proportional to the electric dipole density μ/A at the surface:

$$\Delta\phi(\text{bulk}) = 2\pi\mu/A. \quad (4)$$

Substituting $\Delta\phi(\text{bulk}) = 8.52 \text{ e nm}^{-1}$, we arrive at a dipole density of 1.36 e nm^{-1} at the rutile (110) surface. This result is in reasonable agreement with a value of 1.49 e nm^{-1} calculated from the surface structure of fig. 1.

Within an electrostatic model, one can calculate the energy E_T to transfer an electron from an oxygen atom adsorbed to a surface Ti ion at a surface oxygen coordination site towards this Ti ion by calculating the difference in the electrostatic potential of the surface Ti ion with a formal charge equal to +4 and a point charge -1

Fig. 4. Pauling valencies for nearest-neighbouring Ti^{4+} and O^{2-} sites at different TiO_2 surfaces: (a) rutile (110), (b) anatase (001), (c) rutile (001).

at the adsorbed surface oxygen location and the surface Ti ion with a formal charge equal to +3 and the point charge removed.

This quantity is only indirectly related to the reduction energy, since no driving force, i.e. the difference between the ionization potentials of O^{2-} and the electron affinity of the Ti^{4+} ion itself, is accounted for. However, as long as the non-electrostatic terms contributing to the reduction energy are constant, the surface reducibility is proportional to E_T^{-1} . As far as the rutile (110) and anatase (001) surfaces are concerned, this approximation seems reasonable, since the local environments of five-coordinated Ti^{4+} ions at the rutile (110) and the anatase (001) surfaces are virtually the same (see figs. 1, 2 and also 4).

Since E_T relates to the energy differences due to electron donation from the adsorbate to the surface Ti ion, it will also relate to the Lewis acidity of the Ti surface ion.

We calculated $E_T(Ti^{4+})$ for a coordinatively unsaturated Ti^{4+} ion at the different TiO_2 surfaces. Expressed in terms of electrostatic potentials, $E_T(Ti^{4+})$ becomes

$$E_T(Ti^{4+}) = e[\phi(v) - \phi_0(Ti^{4+})] \quad (5)$$

where $\phi(v)$ and $\phi_0(Ti^{4+})$ are the electrostatic potentials at the vacant surface oxygen coordination site location and its neighboring surface Ti^{4+} ion, respectively. The results, calculated from the data in tables 2–4, are collected in table 6. From these results, it can be concluded that it should be far easier to reduce the five-coordinated Ti^{4+} at the rutile (110) than at the anatase (001) surface. As the Ti^{4+} ion at the rutile (001) surface is four coordinated the quantity E_T^{-1} is not necessarily proportional to the reducibility in this case. Therefore, no definite conclusion

about the reducibility of a Ti^{4+} ion at the rutile (001) surface can be drawn although the E_T value of table 6 strongly suggests, that the reducibility of a Ti^{4+} site at the rutile (001) surface can be intermediate between that of the rutile (110) and anatase (001) surfaces.

It should be noted that the same conclusions can be reached via a very simple consideration using Pauling valencies [12]. Taking into account nearest-neighbour interactions only, and assuming that in both rutile and anatase all Ti–O and Ti–vacancy distances are equal, we can easily deduce the potentials $\phi_0(Ti^{4+})$ at the (coordinatively unsaturated) surface Ti^{4+} ions from fig. 3. The resulting $\phi_0(Ti^{4+})$ values are $-10/3$, $-12/3$ and $-14/3$ (units $e r_0^{-1}$) for Ti^{4+} sites at the rutile (110), the rutile (001) and the anatase (001) surface.

A comparison with table 4 reveals that the $\phi_0(Ti^{4+})$ values occur in exactly the same order as the negatives of the $E_T(Ti^{4+})$ values. This implies that, within the assumption that $-E_T(Ti^{4+})$ and $\phi_0(Ti^{4+})$ are proportional, a calculation of the electrostatic potential $\phi_0(Ti^{4+})$ using Pauling valencies, predicts the correct order of $E_T(Ti^{4+})$ values and surface reducibilities for the (coordinatively unsaturated) Ti^{4+} ions at the surface of anatase and rutile. The assumption involved is consistent, since in the comparison of the $E_T(Ti^{4+})$ values using Pauling valencies, only the nearest-neighbour interactions have to be taken into account. As a consequence, $\phi(v)$ in eq. (5) is a constant and $-E_T(Ti^{4+})$ and $\phi_0(Ti^{4+})$ become proportional to each other.

Of course, the electrostatic theory as it has been applied here is very simple, and thus by no means perfect. It completely neglects important factors like polarization lattice deformation (especially at the surface) and quantum-mechanical effects. However, our simple electrostatic model leads to the prediction that coordinatively unsaturated Ti^{4+} ions at the most densely packed plane of rutile can be more readily reduced than those on the most densely packed plane of anatase. And a similar prediction can be made for the order of intrinsic Lewis activities. From the correlation with Pauling valencies it appears the differences are determined primarily by the different surface arrangement of the Ti^{4+} and O^{2-} ions. The differences in surface potential are dominated by the local environment of these ions notwithstanding the long-range nature of

Table 6

Energies E_T for reduction of a surface Ti^{4+} ion, by an electron located at a neighboring surface oxygen vacancy, as calculated from eq. (5)

	$e\phi(v)$ (rydberg)	$e\phi_0(Ti^{4+})$ (rydberg)	E_T (rydberg)
rutile (001)	0.24 ₇	-2.89 ₇	3.1446 ₈
rutile (110)	0.79 ₇	-2.17 ₃	2.9696 ₂
anatase (001)	0.24 ₃	-3.03 ₂	3.2869 ₈

the electrostatic potential. This conclusion does not only agree with the results presented in this report, but is also supported by the results of electrostatic potential calculations on the bonding of surface oxygen at non-stoichiometric metal oxide phases [13] and on the acidity of natural and synthetic mica-montmorillonites [14].

References

- [1] J. Cunningham, B.K. Hodnett, M. Ilyas, J. Tobin, E.L. Leahy and J.L.G. Fierro, *Faraday Discussion* 72/17 (1981).
- [2] L.G. Svintsova, N.A. Boldyreva and G.P. Korneichuk, *Kinet. Katal.* 18 (1977) 590; Y. Onishi, *Bull. Chem. Soc. Japan* 44 (1971) 912.
- [3] Y. Onishi and T. Hamamura, *Bull. Chem. Soc. Japan* 43 (1970) 996; Y. Onishi, *Bull. Chem. Soc. Japan* 44 (1971) 1460.
- [4] R.W.G. Wyckoff, *Crystal structures* (Interscience, New York, 1963) p. 250.
- [5] R.E. Watson, J.W. Davenport, M.L. Perlman and T.K. Sham, *Phys. Rev. B* 24 (1981) 1791.
- [6] R.J.H. Clark, D.C. Bradley and P. Thornton, *Pergamon texts in inorganic chemistry*, Vol. 19 (Pergamon Press, Oxford, 1973) p. 376.
- [7] E. Madelung, *Physik. Z.* 19 (1918) 524.
- [8] P.P. Ewald, *Ann. Phys.* 64 (1921) 253.
- [9] H.M. Evjen, *Phys. Rev.* 39 (1932) 625.
- [10] F. Berthaut, *J. Phys.* 13 (1952) 499.
- [11] W. van Gool and A.G. Piken, *J. Mater. Sci.* 4 (1969) 95.
- [12] L. Pauling, *The nature of the chemical bond* (Cornell Univ. Press, Ithaca, 1960) pp. 548, 549.
- [13] A. Andreev and N. Neshev, *Kinet. Katal.* 15 (1974) 1097.
- [14] R.A. van Santen, *Recl. Trav. Chim. Pays-Bas* 101 (1982) 157.