Infra-red Studies of Rutile Surfaces

Part 2.—Hydroxylation, Hydration and Structure of Rutile Surfaces.

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A model for the surface structure of rutile is proposed, based on infra-red studies of a crystalline rutile sample prepared by the combustion of Ti(iso-PrO)$_4$. It is suggested that the exterior surfaces of the rutile crystals correspond to three low index crystal planes—namely the (100), (101) and (110). Of these the first two are capable of adsorbing molecular water as a ligand coordinated to Ti^{4+} surface ions, whereas the (110) crystal face adsorbs water dissociatively leading to the presence of equal quantities of two types of OH$^-$ ions. One of these types is associated with a surface Ti^{4+} ion which is five coordinate with respect to lattice oxide ions whereas the other type is bound to a surface Ti^{4+} ion which is only four fold oxide ion coordinate. It is possible to rationalize the observed thermal dehydroxylation and dehydration properties of the oxide and also account for its pyridine adsorption properties.

The concentration, chemical reactivity and infra-red absorption characteristics of the surface hydroxyls carried by metal oxides can be correlated with the coordination of the underlying surface atoms or ions. This in turn leads to the identification of the crystal planes which are present in the oxide's surface.

One of the first attempts at such a correlation was made by de Boer *et al.*[3] for silica; later workers [4, 5] have also considered the surface hydroxylation and structure of this oxide. Anderson and his coworkers [6] used a similar approach in their studies of magnesia surfaces but probably the finest example of the method overall is to be found in Peri's work [7] on the surface structure of alumina. The present paper shows how this general approach may be used to elucidate the structure of the surface of a fine rutile powder such as the WAFLU(2)/800 material used in some of our experimental studies.[1, 2]

THE MORPHOLOGY AND CRYSTAL STRUCTURE OF RUTILE

On the massive scale, rutile is known to crystallise such that the majority (98 %) of the external crystal surface is composed of three planes—the (110), (101) and (100).[8] Of these the first usually has the greatest preponderance (60 %) with the remainder of the surface being composed of the (101) and (100) planes in roughly equal quantities. It is not possible to say precisely what the relative proportions of these surface planes are in fine rutile powders, but there is little doubt that all three are present. It also seems reasonable to suppose that their relative extent will not differ too greatly from the figures given above,[11] because electron micrographs of highly crystalline rutile powders of the type used in the present work—in which the crystal size is ≈ 250 nm—show a morphological resemblance to massive rutile crystals. The choice of crystal planes on which to base a discussion of the surface chemistry of rutile is also more importantly governed by the fact that in the bulk solid the titanium ions are six coordinate with respect to oxide ions. Thus it must

be supposed that the predominating surface crystal planes are those in which the coordination of the surface cations with respect to lattice oxide ions is kept as close to six as possible. In the (101) and (100) planes the lattice oxide ion coordination number is five for the surface cations. The (110) plane contains equal numbers of surface cations which are five and four lattice oxide ion coordinate.

Other planes of low index carry surface cations such that the lattice oxide ion coordination is lower. For example, in the (111) plane the surface cations have only three fold lattice oxide ion coordination. The overall and essential requirement of minimizing the coordinate unsaturation of the surface cations in metal oxides is a fundamental consideration on which a number of successful interpretations of other oxide surface structures have been based,[3-7] and there seems little reason for assuming that it does not hold in the present case.

The crystal structure of rutile is well known.[9] The space group is $P4_2/mnm$ [10] and therefore each titanium ion is a centre of symmetry. This latter point is of primary importance since, in order to relate the results obtained from infrared spectroscopic studies of the surface hydroxyls to the structure of the underlying oxide substrate, it is necessary to have the correct models for each of the postulated surface planes in their hydroxylated or hydrated states. These are best obtained by first determining the structures of the stoichiometric crystal cleavage planes with the appropriate indices and then to add the " elements of water " to each of them in turn. The symmetry consideration mentioned above has the consequence that the correct cleavage planes for the rutile system are those which produce identical faces for each half of the cleaved crystal.

THE (110) PLANE

The (110) cleavage plane is shown in fig. 1. The titanium ions and the shaded oxide ions are coplanar while the non-shaded oxide ions lie above this plane. Adding the elements of water to this face produces a system in which the titanium ions in row A carry a single surface hydroxyl and the neighbouring supra-surface oxide ions in row B accept a proton also to form a hydroxyl ion. This is the form of the hydroxylated surface chosen by other workers [11, 12] to rationalize their experimental data. They recognize two distinct types of hydroxyls on such a surface; those in rows A are monodentate whilst those in rows B are bidentate. However, the method outlined above for obtaining the structure of the hydroxylated surface is but a formal device for obtaining the correct stoichiometry. There is no real constraint to support the implied proposition that the supra-planar oxide ions present in the cleavage model remain in the same locations when the surface carries hydroxyls. As may be seen from fig. 1 the titanium : hydroxyl ratio will be 1 : 1 in both rows A and B when the (110) plane is hydroxylated and, since the surface layers of rutile are predominantly ionic in character, the most reasonable arrangement would seem to be that which places the oxygens of the OH^- species close to the surface cations but away from the anions. On this basis the structure of the hydroxylated (110) face is such that the OH^- ions lie directly above the surface cations with their axes—aligned by the electrostatic field—perpendicular to the surface. Arrayed in this way the OH^- ions in row A are above Ti ions that are five fold coordinate with respect to lattice oxide ions whilst those in row B are above cations that are otherwise only four fold coordinate.

Considering the results shown in the previous paper,[2] especially those concerned with pyridine adsorption, there are only two absorption bands (at 3410 and 3650 cm^{-1}) not ascribable to molecular water. Using similar principles to those enunciated by

Peri,[7] we propose that the 3410 cm^{-1} absorption corresponds to the fundamental stretching frequency of the row B OH$^-$ ions and the 3650 cm^{-1} absorption similarly to the OH$^-$ ions in row A, the lower frequency manifest by the former species being due to the greater reduction of its O—H σ-bond strength by the relatively greater coordinate unsaturation of the underlying Ti ion. It is noticeable that the fundamental stretching frequencies of both OH species in this oxide are lower than those observed for the hydroxyls on silica where the bonding is predominantly covalent.[13]
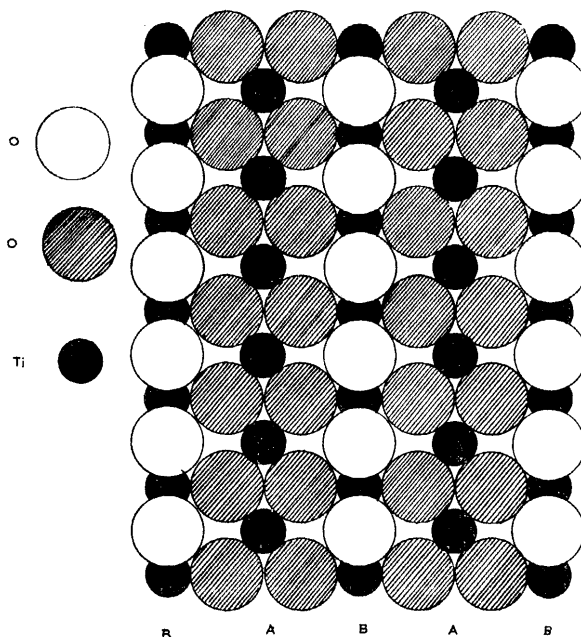

FIG. 1.—A plan view of the (110) cleavage plane of rutile. There are 10.2 Ti ions nm^{-2}.

Another feature of the model proposed here is that although the OH$^-$ ions are closely spaced (A—A = B—B = 0.296 nm, A—B = 0.36 nm) hydrogen bonding interactions would not be expected to occur. The OH$^-$ ions are coplanar with their axes parallel, thereby preventing interaction of the hydrogens with neighbouring oxygens. In contrast, if the first model is considered in which the row B OH$^-$ ions are bidentate,[11, 12] then their oxygen atoms would be closer to the plane of the surface Ti ions than the oxygen atoms of the row A hydroxyls. Such an array would be similar to the one present on the hydroxylated (100) face of magnesia [6] and as such would place the hydrogen atoms of the rows B hydroxyls sufficiently close to the oxygen atoms of the rows A OH$^-$ ions to produce a hydrogen bonding interaction.

Thus the spectrum of this surface structure would also exhibit two infra-red absorption bands with that at lower frequency corresponding to the perturbed bidentate hydroxyl. It would also be expected however, that the lower frequency absorption band would be broad. Both the 3650 and 3410 cm^{-1} absorption manifest by the rutile surface [1, 2] are narrow and of equal width.

THE (101) PLANE

The (101) cleavage plane of rutile is shown in fig. 2. The Ti ions are coplanar and five coordinate with respect to lattice oxide ions. The latter are positioned so

that the shaded circles represent oxygens laying beneath the plane of the Ti ions whereas the open circles correspond to oxygens laying above the " Ti plane ". The dissociative chemisorption of water on this face would result in each surface Ti ion carrying two hydroxyls with a surface concentration for the latter of 15.9 nm^{-2}. Since the cross sectional area of an OH$^-$ ion is about 1×10^{-1} nm^2, this possibility may be excluded and it seems more reasonable to suppose that the inherent coordinate unsaturation of each of the surface cations is offset by the adsorption of water as a σ-bonded ligand using a filled $a_1(s,p_\sigma)$ orbital of the water molecule's oxygen atom in conjunction with an empty orbital on the Ti ion to form the bond. Held in this way, the oxygen atom of the water molecule may be considered to complete the octahedral coordination shell of the cation which lies on the two fold symmetry axis of the H—O—H system. As can be deduced from fig. 2, and seen more readily from the appropriate crystal model, such a system directs the hydrogens away from the surface oxide ions and minimizes the possibility of intermolecular hydrogen bonding between the water molecules. In consequence the water molecules would be expected to exhibit absorption bands due to each of their three normal modes of vibration.[14] The frequencies of the bands corresponding to the v_1 and v_3 absorptions would be expected to be lower than those observed for a free water molecule, but their relative intensities and separation might be expected to remain about the same. In contrast, on the basis of a Walsh type diagram,[18] the frequency (v_2) of the deformation vibration would be expected to be slightly greater than that observed for the free molecule.[14, 15]
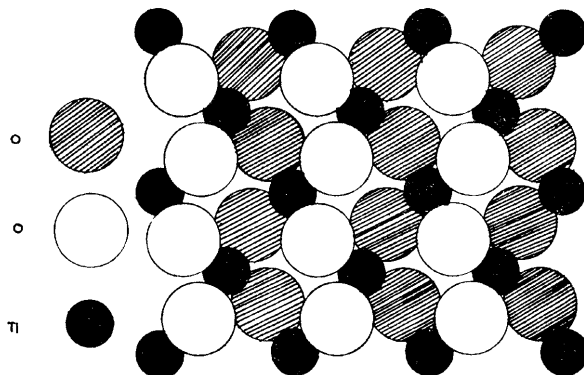

FIG. 2.—A plan view of the (101) cleavage plane of rutile. There are 7.9 Ti ions nm^{-2}.

Noting the results presented previously [2] we therefore suggest that the absorption bands at 3680 and 3610 cm^{-1}—which always behave as a pair—correspond to the v_3 and v_1 frequencies of molecular water held on the (101) face in the manner described above. In particular it is noticeable that when pyridine is absorbed on the 473 K outgassed surface the disappearance of these two bands from the 3000-4000 cm^{-1} region is accompanied by the disappearance of the small residual absorption band centred about 1610 cm^{-1}.

THE (100) FACE

The (100) cleavage plane of rutile is shown in fig. 3. The cations are coplanar and five coordinate with respect to lattice oxide ions. The shaded circles correspond to oxide ions laying beneath the plane carrying the cations ; the open circles represent supraplanar oxide ions. Dissociative addition of the elements of water to this

cleavage model would lead to a structure in which each Ti ion carried two hydroxyls with a concentration of 14.7 OH^- nm^{-2}. As for the (101) face such a possibility must be excluded; in this case also it is more reasonable to suppose that in the hydrated or hydroxylated state the sixfold coordination of the surface cations is completed by the oxygen atom of a water molecule adsorbed in a similar manner to that described for the (101) face. Held as a coordinating ligand in this way the plane of the H—Ô—H system is at a low angle to the (100) plane; an arrangement that places the hydrogen atoms sufficiently close to the neighbouring supraplanar oxide ions to promote a hydrogen bonding type of interaction (see fig. 3B). From our previous work,[2] when rutile is outgassed at ambient beam temperatures there is a broad absorption band centred about 3550 cm^{-1} which is associated always with absorption centred about 1610 cm^{-1}. The 3550 cm^{-1} absorption is therefore clearly caused by molecular water on the surface and the position and broadness of the band implies that the corresponding species is perturbed by an interaction of the hydrogen bonding type. We therefore suggest that the 3550 cm^{-1} absorption corresponds to a fundamental OH stretching absorption of molecular water adsorbed on the (100) face.
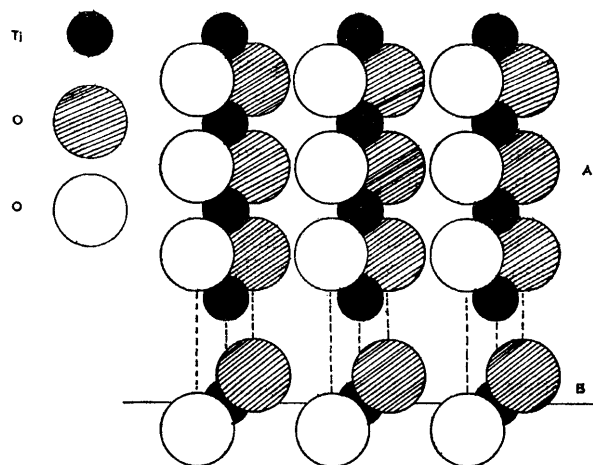

FIG. 3.—(a) A plan view of the (100) cleavage plane of rutile. There are 7.4 Ti ions nm^{-2}. (b) An elevation looking along the c-axis in the line of the (100) cleavage plane.

THE DEHYDRATION AND DEHYDROXYLATION OF RUTILE SURFACES

THE (100) AND (101) SURFACE PLANES

The following has been taken as a fundamental tenet; that the ease of removal of water from a hydrated or hydroxylated surface is governed by the difference in energy between the hydrated and dehydrated states and not solely by the " strength " of binding of the hydroxylic species.

In the rutile structure the Ti ions are octahedrally coordinated but the octahedron is distorted so that the apical oxygens (a) are farther from the central cation than those (s) at the corners of the square plane (Ti—O(a) = 0.1988 nm and Ti—O(s) = 0.1944 nm). On the basis of the model described above, the oxygen atoms of the water molecules adsorbed on the (100) face are each sited at the apical positions of the coordinating octahedra. In consequence their removal, although leaving the surface cations coordinately unsaturated would not correspond to a process so

energetically unfavourable as removal of water molecules from above Ti ions in the (101) plane, where the oxygen atom of the ligand occupies one of the square plane positions. It is possible on this basis to rationalize the experimental result [2] that raising the outgassing temperature of the oxide above ambient first leads to the disappearance of the 3550 cm^{-1} absorption band following under more stringent temperature conditions by the concomitant disappearance of the 3680 and 3610 cm^{-1} absorptions.

THE (110) SURFACE PLANE

The distance between neighbouring OH$^-$ ions on the (110) face is 0.296 nm when they are in the same row (A—A, see fig. 1) and 0.36 nm when in adjacent rows (A—B). It seems reasonable therefore to suppose that the easiest mode of dehydroxylation is elimination of water between adjacent OH$^-$ ions within the same row,

$$\text{i.e. } 2OH^- \rightarrow H_2O \uparrow + O^{2-}. \tag{1}$$

Elimination of water in this way for row B leaves the oxide ions sited between Ti ions that are otherwise four coordinate, whereas the same process for row A leaves the oxide ion to be shared between Ti ions that are five coordinate with respect to lattice oxygens. We have therefore assumed that the OH$^-$ ions in rows B will be the more readily lost on raising the outgassing temperature. A Monte Carlo statistical analysis [7] shows that it is possible to remove 81 % of the row B OH$^-$ ions by elimination of water between adjacent pairs. Removal of the remaining " isolated" hydroxyls in rows B can only be achieved by condensation with a neighbouring row A OH$^-$ ion. On the basis of the present model the 3410 cm^{-1} absorption band is that which is associated with the rows B OH$^-$ ions. The experimental results described previously [2] indicate that on steadily raising the outgassing temperature most of this absorption band is removed whilst the intensity of the absorption at 3680 cm^{-1} (row A OH's) is unaffected, although the complete disappearance of the 3410 cm^{-1} band is always accompanied by a reduction in the absorption intensity of the 3680 cm^{-1} band.

There are two other general features worthy of note. First, the relative ease of dehydroxylation of the rutile surface as compared to that found for alumina, magnesia and silica.[3-7] Probably the greater density of the rutile crystal leads to a relatively lower energy of the incompletely coordinated cations formed on dehydroxylating the rutile surface. Secondly, and most important, there is no report in the literature of any study on 100 % pure rutile. All the samples studied have contained between 1-3 % of anatase, and there is therefore the possibility that the surfaces of the oxide samples studied both by ourselves and the other workers quoted have corresponded in fact to a superficial layer of anatase carried on a rutile substrate. In the present case the X-ray diffraction evidence is against this, since both the rutile and anatase diffraction patterns are clearly observed; if the anatase were present as a necessarily thin superficial layer a less clear pattern for this crystalline form might have been expected.

This general comment is not intended to cast doubts on the present work nor on that of others. Indeed, even if the adverse situation broached above were eventually found to exist it would not necessarily negate the conclusions reached in this or in other papers. A comparison of the rutile and anatase structures [16] shows that in each polymorph the fundamental structural unit is the TiO$_6$ octahedron—with similar Ti—O distances in each case. The difference between the two structures arises from the different packing of these octahedra although this difference is not of type to markedly alter any of the essential features of the model described here. That

is to say that the infrared spectrum of the hydrated/hydroxylated anatase surface would still be expected to exhibit absorption bands due to OH^- ions sited on surface cations otherwise four or five oxide ion coordinate and so on.   There is moreover no reason to suppose that the absorption frequencies of the corresponding bands would be different for the same species carried on rutile.   Unfortunately, in the present state of the literature, it is not possible to ascertain whether this is so, since most of the anatase samples studied have had rather a high silica content, as evidenced by their relatively high absorption intensity at about 3725 cm^{-1} (see for example re.f (17)).

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