

## SURFACE CHEMISTRY OF OXIDES

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**Abstract**—The chemistry of the surface of oxides depends to a large extent on the quantity and type of both physically and chemically (OH groups) adsorbed water. Infrared spectroscopy coupled with a variety of chemical exchange processes has provided useful information on the nature and stability of the adsorbed species, and on the interaction of the surface hydroxyl groups with adsorbates at the solid/vapour and solid/liquid interfaces. Electrochemical techniques are used to study the oxide/aqueous solution interface to provide surface charge data and establish zero points of charge, both of which are related to the character of the hydroxyl group and its environment. This paper briefly reviews the application of these methods to the oxides of titanium, silicon and aluminium, in both the pure and mixed forms, and to the study of the deposition of one oxide on the surface of another.

Oxide powders are used in a wide variety of technological processes and in many cases the chemistry of the surface plays a predominant role. During the last decade there has been a significant increase in fundamental work on oxide surfaces and this has led to a better understanding of the relationship between the surface chemistry of oxides and the specific character of their surfaces. This was the subject of the Faraday Society Discussion No. 52 held at Brunel University in 1971. It is a very broad subject and impossible to review adequately in one paper, so I will restrict discussion primarily to the use of i.r. spectroscopy and electrokinetics in the chemical characterisation of oxide surfaces and show how these techniques have provided important information for the manufacture and application of oxide powders. It will only be possible to refer to a limited amount of work in this field, the selection of which will serve to illustrate the vital points. We shall concentrate on alumina, silica and titania, important oxides in the pigment and catalyst industries.

The chemistry of the oxide surface is, to a large extent, dominated by the hydroxyl groups, which arise from the interaction of water vapour with the surface planes to achieve valency saturation. To explicitly define the surface, it is necessary to determine the number of such groups, their dissociation behaviour and the nature of their interaction with the components of the surrounding medium. The literature contains a large amount of i.r. spectroscopic data on oxide surfaces.<sup>1,2</sup> The technique has been successfully used in defining the conditions for dehydroxylation and their replacement, as well as when combined with other techniques providing a means of differentiating between hydroxyl groups in different environments. Interaction with specific adsorbates gives a measure of the type of bonding in which the hydroxyl group may be involved, and also provides information on the acidity of the surface in terms of Lewis and Brønsted sites.

In the interpretation of i.r. spectra the question arises as to how much of the geometry of the bulk crystal is reflected in the surface. The problem of defining the crystal planes is well illustrated by published data on titanium dioxide. Several authors have used only one plane, the predominant one, to identify i.r. bands (Boehm,<sup>3</sup> Primet *et al.*,<sup>4</sup> Jackson and Parfitt<sup>5</sup>), but perhaps the most successful interpretation has been made by Jones and Hockey<sup>6</sup> who, following Rutley's Elements of

Mineralogy,<sup>7</sup> assume that most of the external surface is composed of three planes, the (110), (101) and (100), with 60% of (110) and the remainder approximately equally divided between the other two. Nevertheless, it will continue to be argued that the fine crystallites used in i.r. studies on oxide powders may far from reflect the structure of the macro crystal.

Various studies of the concentration of surface hydroxyls on silica (using thermogravimetric, spectroscopic and chemical techniques) indicate that after outgassing at 150–200°C to remove physically adsorbed molecular water there are about five hydroxyl groups per nm<sup>2</sup> of surface corresponding to one hydroxyl per silicon atom in the surface.<sup>8</sup> There has been speculation as to whether this number represents the concentration on a fully hydroxylated surface since to define the latter it is necessary to assume the nature of the crystal planes that predominate in the surface, e.g. the rhombohedral face of  $\beta$ -tridymite has 4.6 silicon atoms per nm<sup>2</sup> whereas the (100) face of  $\beta$ -cristobalite would be fully hydroxylated with each silicon atom carrying two hydroxyl groups giving a theoretical maximum of 7.9 hydroxyls per nm<sup>2</sup>. In a study by Hockey *et al.*<sup>9</sup> of the stoichiometry of the reactions of SiMe<sub>2</sub>Cl<sub>2</sub>, TiCl<sub>4</sub> and BCl<sub>3</sub> with silica hydroxyl groups it was demonstrated that the fully hydroxylated surface contains two distinct types of hydroxyl sites. These are single hydroxyls at  $1.4 \pm 0.1/\text{nm}^2$  and interacting (hydrogen-bonded) hydroxyls in pairs at  $1.6 \pm 0.1/\text{nm}^2$ , giving a total population of  $4.6/\text{nm}^2$ . The hydrogen-bonded groups are lost by outgassing at about 500°C while the concentration of single hydroxyls remains approximately constant up to about 600°C. Further loss of hydroxyls occurs at higher temperatures but the details are not well defined. At room temperature evacuation is likely to lead to some dehydroxylation but again there is no definitive evidence. To explain these numbers it is necessary to consider that the surface corresponds to an array of different crystal planes, some with hydroxyls sufficiently far apart to preclude hydrogen-bonding and others with hydroxyl groups close enough to interact. A silica surface evaluated at high (>800°C) temperatures is not re-hydroxylated to a significant extent when brought into contact with a saturated water vapour at room temperature, although at lower outgassing temperatures the hydroxylation process is, to some extent, reversible.<sup>10</sup> However, the exact

behaviour of a particular silica depends on its nature and previous treatment. It would be fair to say that of the oxides considered here silica is the simplest in terms of the behaviour of its hydroxyl groups but it has taken a long time to establish a satisfactory quantitative picture.

For titanium dioxide the situation is becoming clearer. A number of papers have been published by Parfitt *et al.*,<sup>5,11-13</sup> Jones and Hockey<sup>6,14,15</sup> and Primet *et al.*<sup>4,16,17</sup> describing i.r. investigations on the titania surface. Although there are some differences in detail in the assignments between the authors there would now seem reasonable justification for assuming that on the surface of rutile two distinct types of isolated hydroxyl group exist in different stereochemical environments. Parfitt *et al.* conclude that one of these is associated with a metal site having monodentate attachment (terminal OH) and the other on an oxide site with bidentate attachment (bridged OH). Jones and Hockey's interpretation is different—they postulate that one of the hydroxyls is associated with a surface  $Ti_4^+$  ion which is five-coordinate with respect to lattice oxide, and the other with a four-coordinate surface titanium site. There is general agreement that complete removal of molecular water from the plane surface requires outgassing  $\geq 200^\circ C$  after which treatment the surface contains  $3 \pm 1$  hydroxyls per  $nm^2$ , about a quarter of the theoretical saturation value.<sup>18</sup> The surface is virtually free of hydroxyl groups after outgassing at  $450-500^\circ C$ .<sup>18</sup> Two types of water are thought to exist on the titania surface, one being hydrogen-bonded and removed by outgassing at room temperature, while the other is coordinately bound and requires a higher temperature. Jones and Hockey<sup>15</sup> successfully related experimental data to their model involving the (110), (100) and (101) planes, the former being fully hydroxylated while the latter two contain no hydroxyl groups. The effect of outgassing on the surface chemistry of rutile has been admirably illustrated by heats of immersion and electrophoretic studies. An increasing heat of immersion in water with increasing outgassing temperature was demonstrated by Zettlemoyer *et al.*,<sup>19</sup> a maximum value being reached at about  $250-350^\circ C$ ; the lack of consistency in published data available at the time (1966) shows how much surfaces can vary with method of manufacture and pre-treatment. The particular electrophoretic studies under consideration involved titania in pure alcohols, heptanol<sup>20</sup> and pentanol.<sup>21</sup> In both cases a very definite maximum in zeta potential occurred at about  $200^\circ C$  by which temperature it was supposed that all molecular water is removed from the surface. An explanation for the marked decrease in potential at higher temperature is not immediately obvious from the available data.

For alumina the picture is even more complex. Five different isolated hydroxyls were identified by Peri,<sup>22</sup> who using Monte Carlo methods predicted that these could occupy different positions in the lattice adjacent to differing numbers of surface oxide ions from 0 to 4.

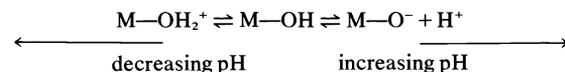
The acidic nature of oxide surfaces has been established from i.r. spectroscopy of adsorbed amines. Ammonia and pyridine are commonly used, having quite different strengths hence providing a range in selectivity in reactions with surface sites. It would appear from the literature that in these reactions pure oxides normally exhibit only Lewis acidity while mixed oxides show appreciable Brønsted acidity. Experiments with silicas indicate that ammonia and pyridine only hydrogen-bond with the surface since there is no evidence of interaction with Lewis or Brønsted acid sites.<sup>23,24</sup> The spectra of pyridine adsorbed on alumina show bands characteristic

of coordination to Lewis acid sites with no evidence for the pyridinium ion that would be present if the surface exhibited Brønsted acidity.<sup>23</sup> Similarly with pure rutile, for which the spectra of adsorbed ammonia indicates coordination to two different cation sites,<sup>12</sup> only one of which is sufficiently strong to coordinate with the weaker base pyridine.<sup>13</sup> However, Primet *et al.*<sup>17</sup> observed that trimethylamine, a stronger base, adsorbs on a  $200^\circ C$  evacuated anatase surface to give i.r. bands characteristic of the  $NH^+$  group indicating some Brønsted activity.

I.R. spectra for mixed oxides present a much more difficult picture for interpretation. A variety of methods have been used in the preparation of the mixed oxides and therefore the constituents of, say, a silica/alumina system are likely to be present in various stages of intermixing ranging from perfect alternation of silica and alumina to regions containing bulk silica or bulk alumina. Both Lewis and Brønsted acidity have been detected by pyridine adsorbed on silica/alumina catalysts, and the conversion of Lewis sites on a dehydrated surface to Brønsted sites by adding water vapour is well known.<sup>1</sup> Pitkethly *et al.*<sup>25</sup> describes the preparation of two silica/alumina systems, one in which the aluminium atoms are incorporated (by ion-exchange) on to a silica surface, and another in which the aluminium is co-precipitated with the silica so that it is incorporated into the lattice. In both cases the aluminium atoms have only oxygen and silicon atoms as near neighbours and are therefore potential catalytic sites. Using pyridine, it was demonstrated that, for the aluminium sites in the first system, there is both Lewis and Brønsted acidity, the amount of each depending on the pre-treatment and surface water content; the conversion of Lewis acid sites to Brønsted sites is reversible. However, when the aluminium is buried within the silica, only Brønsted sites were detected after dehydration, suggesting that, after heat treatment, protons are retained within the lattice in the vicinity of the aluminium. These slowly migrate to the surface when water is present, forming pyridinium ions with adsorbed pyridine. Thus i.r. studies using pyridine provide an effective method for locating the position of aluminium in the silica/alumina lattice, and also for defining potential catalytic activity, both being of relevance to the coating of titanium dioxide pigments.

I.R. studies at the solid/liquid interface are becoming particularly valuable in the investigation of interactions at the surface that are relevant to paint and related systems. A good example of the potential of this technique is Rochester's recent study of the adsorption of unsaturated long chain carboxylic acids on silica from carbon tetrachloride solutions.<sup>26</sup> Interactions between surface and alkene residue and between hydroxyl and carboxylic acid groups, are identified giving important information on the orientation of the adsorbed molecules at the solid/liquid interface.

The surface chemistry of an oxide surface in contact with an aqueous solution is determined to a large extent by the dissociation of the hydroxyl groups. The equilibria may conveniently be expressed as



which indicates that by appropriate adjustment of pH the surface may carry either a positive or negative charge, while at an intermediate value the hydroxyl groups are undissociated, and the surface has zero charge. This "point of zero charge" (pzc) more correctly defines the situation

when there is net zero charge on the surface, and is readily determined by potentiometric titrations. The pH at the pzc has a specific value for each oxide depending on the electronic character of the metal-oxygen bond and the degree of stoichiometry of the surface. Parks<sup>27</sup> has reviewed the pzc values for oxides, and show typical values for SiO<sub>2</sub> of pH 1–2, TiO<sub>2</sub> pH 5–6 and Al<sub>2</sub>O<sub>3</sub> pH 8–9. Microelectrophoresis provides a useful tool for establishing the pH at which the oxide particles do not move in an electric field. This is called the isoelectric point (iep) and is equal to the pzc when no specific adsorption occurs in the Stern layer. A recent review<sup>18</sup> of zero point data, from electrokinetic and titration experiments, for titanium dioxide gives the following average values

|         |     |     |     |            |
|---------|-----|-----|-----|------------|
| Rutile  | pzc | 5.3 | iep | 4.8 or 5.6 |
| Anatase | pzc | 6.2 | iep | 6.1        |

Two results are quoted for the iep of rutile since there are about an equal number of data around the two values. Examination of all the results shows clearly the effect of surface impurities which are probably carried forward from the preparation. Adsorbed anions reduce the isoelectric point<sup>28</sup> and both sulphate and chloride ions are normally present on the surface of titania particles prepared by the sulphate and chloride processes respectively. The effect of such impurities on the electrochemical behaviour of oxide surfaces has not been sufficiently recognised in the past, hence many of the literature zero point data do not accurately reflect the pure oxide. The author's review<sup>18</sup> of TiO<sub>2</sub> suggests that there is a real difference between rutile and anatase, corresponding to about one pH unit.

Microelectrophoresis has already proved valuable in studies of the behaviour of oxides in solutions containing hydrolysable species, which is a system that has great technological significance in mineral flotation, water clarification, pigment and catalyst preparation etc. It may be used to directly observe charge reversal on adsorption, and when a new hydrated oxide is precipitated onto the oxide substrate the chemical character of the coated surface may be defined from the changes in electrophoretic mobility with pH. From a series of experiments with SiO<sub>2</sub> and TiO<sub>2</sub> in solutions of Co(II), La(III) and Th(IV) salts James and Healy<sup>29</sup> identified three charge reversals which in order of increasing pH correspond to the (a) isoelectric point of the substrate, (b) the pH of surface nucleation of the metal hydroxide, assumed to be induced at a lower pH than for bulk precipitation by the electric field of the surface, and (c) the isoelectric point of the metal hydroxide coating. A similar shift in isoelectric point from pH 5.9 to pH 9 was observed with TiO<sub>2</sub> in Al(NO<sub>3</sub>)<sub>3</sub> solutions corresponding to progressive nucleation of the aluminium hydroxide coating.<sup>30</sup> The application of electrophoresis to more complex precipitation phenomena involving TiO<sub>2</sub> has been described by the author,<sup>31,32</sup> and demonstrates the value of the technique, particularly to pigment and catalyst preparation and characterisation.

Microelectrophoretic data of silica coated TiO<sub>2</sub> indicate that the surface has similar electrochemical character, in terms of the isoelectric point, to that of normally precipitated hydrous silica whether the silica coating is formed by nucleation and growth on the substrate surface or by coagulation onto the surface of silica particles formed in the liquid phase. But the method gives little other information on the nature of the coating. Two

further aspects are important, both concerned with the penetration of molecular/ionic species into the silica layer. Zettlemoyer *et al.*<sup>19</sup> measured nitrogen and water vapour adsorption on silica coated rutile prepared in a manner which is known to produce a uniform and compact surface layer. The surface was found to be non-porous to nitrogen but porous to water vapour. Heats of immersion in water of surfaces containing increasing amounts of silica show the anticipated decrease, when calculated on the basis of the water areas (not on the normal BET N<sub>2</sub> area), from 1070 ergs/cm<sup>2</sup> for pure rutile to 485 ergs/cm<sup>2</sup> for a 15% SiO<sub>2</sub> coating. These values are somewhat higher than those normally associated with the pure oxides, and probably reflect an uncertainty in the water areas for the porous surface. However, silica is known to be unique among the oxides in terms of its electrochemical character (surface charge-pH and total double layer capacitance behaviour),<sup>33</sup> and the exceptionally high charge densities are consistent with the proposal that the surface is porous to both potential determining and counterions. The presence on the surface of BDH precipitated silica of a gel layer which is non-porous to nitrogen, was demonstrated by tritium exchange by Yates and Healy.<sup>34</sup> This gel layer must be sufficiently compact when dry to be non-porous to nitrogen but swell in solution to allow ions to penetrate freely. Heating the silica removed the porosity to counterions at 500°C and to both protons and counterions at 800°C. For a complete analysis of the silica coating it is therefore necessary to combine electrophoresis with potentiometric titrations, tritium exchange, dissolution and gas adsorption, and such a comprehensive study has not yet been reported.

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