PHOTO-INDUCED PROCESSES AT TITANIUM DIOXIDE SURFACES

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ABSTRACT. Evidence is presented to demonstrate the participation of surface hydroxyl groups in the photosorption of oxygen on hydroxylated rutile (TiO₂) surfaces under the stimulation of near u.v. radiation (310nm < λ). Species resembling adsorbed hydrogen peroxide are produced which have the capability of interacting with dinitrogen in a consecutive thermal process.

Introduction

Interest in the uses of titanium dioxide in photocatalysis and in photoelectrochemistry has become widespread, since the photoelectrochemical experiments of Fujishima and Honda (1) demonstrated the photoelectrolysis of water into its constituent elements. As testimony to the efforts which have been made subsequently to design a satisfactory system which might utilise solar energy to drive the electrolysis of water, and moreover to the dominant use of TiO₂ and related mixed oxides, reference need be made only to the published proceedings of successive International Conferences on the Photochemical Conversion and Storage of Solar Energy. (2)

In the context of research on Heterogeneous Photocatalysis recent reviews of the subject by Formenti and Teichner (3), and by Bickley (4), and the published proceedings of the N.A.T.O. A.S.I. on Photoelectrochemistry, Photocatalysis and Photoreactors (5) gives an excellent means of identifying the common factors in these popular but difficult areas of research.

In this presentation evidence will be given to emphasise the importance of hydroxylated surfaces of titanium dioxide (rutile) in some aspects of heterogeneous photocatalysis. It should be stressed that the presence of adsorbed water is not essential for TiO₂ to behave as a photocatalyst but that in situations in which it is present it can exert a dominant effect. Of particular interest are those photochemical processes which may be possible in the natural environment of the Earth's surface and which may be stimulated by direct solar radiation. Examples of such processes are:- the photosorption of oxygen (6), the photo-synthesis of hydrogen peroxide (7), the

oxidative photo-fixation of atmospheric dinitrogen (8) and the photo-oxidative degradation of numerous organic molecules to form CO₂ (9).

Experimental

The experiments, which are described, were performed in a vacuum system which was capable of attaining ultimate low pressures of ca. 10⁻⁴ Pa. Measurements of adsorption were made in a small constant volume section of the apparatus (240 cm³) which contained the adsorption cell and two pressure gauges; a Pirani gauge and a pressure transducer (Bell and Howell Ltd. 0-35 mb A). The constant volume system could be connected to a pair of mercury filled gas burettes (300 cm³) by which experiments at constant pressure could be achieved. Gas analyses were made by releasing the contents of the adsorption system through a calibrated needle valve into a magnetic deflection mass-spectrometer (Vacuum Generators, Micromass 2A) which was capable of detecting molecules with relative masses of 2, 3, 4, 12-60 and 48-240.

The adsorption cell, into which about 0.51 of the TiO₂ specimen was usually placed, was constructed of clear silica tubing (Ø=30 mm) to which a silica side-arm and two Vitreosil clear silica optical windows were fused. Irradiation of the surface of the powdered specimens was effected from above by a 500W medium pressure mercury arc contained within a water cooled pyrex glass condenser.

Analyses of the strongly adsorbed surface species were made using temperature programmed desorption (t.p.d.) linked to continuous monitoring of the gas phase using the mass-spectrometer in its scanning mode of operation.

The materials used in this work were as follows:-

1) All gases were supplied in pyrex glass bulbs (1 dm³) and were designated as spectrometrically pure by the manufacturers, British Oxygen (Gases) Ltd.

2) The TiO₂ was supplied by Tioxide International Ltd. according to the following specifications; a) a low area rutile, ex sulphate of 4.2 m²g⁻¹ containing Si 300 ppm, Fe 3 ppm, Al₂O₃ 13 ppm, K₂O 20 ppm and CaO 13 ppm

b) a higher area material, ex chloride hydrolysis of 20.2 m²g⁻¹ containing Si 100 ppm, CaO 60 ppm, Fe 6 ppm, K₂O 18 ppm, ZnO 23 ppm and Al₂O₃ 33 ppm

3) H₂O₂(1) was supplied by BDH Ltd.; 30 volume.

4) HSO₄(1) was obtained from a laboratory deioniser with a conductivity of 1.3 x 10⁻⁴ Ω⁻¹ m⁻¹

Results

Figure 1 depicts the photosorption of O₂ upon rutile (TiO₂) surfaces. The results show the extent of the photoadsorption during continuous illumination, and the kinetic profiles approximate to first order behaviour. Most significantly is demonstrated the effect of progress-