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Heterogeneous photocatalysis at liquid–solid interfaces. Oxidative dehydrogenation of propan-2-ol as a method of assessing photocatalytic activity?

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ABSTRACT

Heterogeneous photocatalysis has developed significantly since its discovery about 100 years ago. Using the number of published papers as an index, the subject progressed slowly in the first 50 years, since which it has become much more prolific. Accompanying the increase in publications has been increases in the number of research centres undertaking studies in this area with diversities of reactions studied, light sources used, photocatalytic materials prepared, and experimental conditions adopted. The quantification of kinetic data, in the form of reaction rate constants and quantum efficiencies, has been inevitably subject to variability as a consequence. In an attempt to overcome these limitations, it was suggested by Bickley (1980), and reiterated by Teichner (1985) that a standard calibration reaction should be used to reduce the variability. Criteria for a standard reaction should be an intrinsic chemical simplicity, product analysis by a widely available method, and the use of a commonly available photocatalytic material. Progress has been made towards achieving these objectives, with the oxidative dehydrogenation of propan-2-ol to propan-2-one at powdered titanium dioxide surfaces being one method currently considered suitable for this purpose. The attractiveness of this reaction is that propan-2-one can be quantified below micro-molar concentrations by gas–liquid chromatography, a widely available technique. Furthermore the kinetic behaviour of this photocatalytic reaction is strictly pseudo-zero-order for a diverse range of titanium dioxide preparations. The objective of this article is to describe the main features of a carefully controlled investigation of this reaction and, as a result, other features are revealed that suggest the conditions under which it is used for the purposes of calibration should be carefully defined.

1. Introduction

Photocatalysis has its origins in the early years of the twentieth century [1,2] since when its scope and understanding have developed widely. Until about 1960, relatively few papers (381) had been published which could be described as reporting photocatalytic phenomena, and the titles of papers relating to it did not contain the explicit description of heterogeneous photocatalysis until 1964, when Doeffler and Hauffe [3] used the term in describing the photo-electronic behaviour of zinc oxide. A consequence of a landmark publication by Fujishima and Honda [4] in which the photo-electrolysis of water was addressed, was an upsurge of interest in analogous phenomena, including heterogeneous photocatalysis, which has proliferated since that time. Currently a SciFinder search of the published literature produces a total of 56,378 published articles, with in excess of 52,000 arising in the last 25-year period (1985–2010).

The manner in which interest in heterogeneous photocatalysis was increasing, led the present author, in 1980, at the 3rd International Conference on the Photochemical Conversion and Storage of Solar Energy in Boulder, Colorado, and S.J. Teichner in 1985, at a NATO Advanced Study Institute in Maratea, Italy, to urge the exercise of care in publishing work that did not contain a means of comparing data with those of others, possibly through the use of a standard photocatalyst, and a move towards achieving this objective was made by a Specialist Commission of IUPAC which consolidated definitive terms relating to the subject. Several photocatalytically induced processes have since been considered as standard reactions, among which are included the first-order decolourisation of methylene blue, and the zero-order photo-oxidation of propan-2-ol, both at liquid/solid interfaces; the latter reaction also being applicable at the vapour/solid interface [5–7].

Making comparisons through a standard reaction has the potential to enable the standard photocatalytic rate measurements with a set-up particular to the needs of any project, and, as long as the reactor system does not undergo physical changes between sets of measurements, the relative performance of the system for chemically distinct processes should be possible. Too often in the past

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studies have been conducted using poorly defined materials, often arising from their different methods of manufacture, and their use has enabled the chemical pathways of new reactions to be identified, but the accompanying rate data and quantum efficiencies were most probably influenced by the intrinsic characteristics of the experimental systems.

One purpose of this paper is to encourage the use of standard reactions to obtain better uniformity in photocatalytic studies. Such standardisations can only be effectively achieved through the use of a photocatalyst that is generally available on a world-wide basis, and which maintains its activity within, and across, the sources of its supply. Additionally, its purchase cost should not make it prohibitively expensive to use.

Likewise the choice of a standard reaction should render it easily accessible, through the use of readily available analytical methods. Thus the study of the decolourisation of methylene blue can be easily followed by UV–visible spectroscopy, while with propan-2-ol photo-oxidation the use of gas–liquid chromatography can enable the detection of the formation of propan-2-one in nano-mole quantities.

Variability between sets of data often occurs from the use of different sources of UV radiation [8]; UV-A/B, medium and high pressure mercury or mercury–xenon arcs, UV-C, low pressure mercury arc and black lights, UV LEDs, radio frequency activated electrode-less discharges etc. Indeed the reactor/photon source geometry may differ through the use of externally positioned sources producing asymmetrical reactor radiation fields, or internally positioned ones leading to more symmetrical radiation fields. Additional variations arise from the operational lifetime of a particular source that affects both the photonic output (flux), and the spectral distribution.

A further objective is to demonstrate the reliability of the photocatalytic oxidation of propan-2-ol to propan-2-one in the liquid phase, and to use this as a basis for identifying factors that may present problems during its use as a standard. Indeed, while passing mention will be made of other standard processes (e.g. decolourisation of dyestuffs), some factors that emerge are common to each process.

2. Experimental

2.1. Reactor

Details of the microreactor system used in the present work have been previously described elsewhere [6]. The sealed reactor, containing a charge of 200 cm^3 of pure liquid propan-2-ol, and a magnetic stirring bar (1 cm length), was placed in a thermostatically controlled water bath (24 ± 0.5 °C) fitted with 2 mm-thick quartz-plate side windows, enabling a collimated/parallel beam of UV radiation from a point source (Oriel Model 66011), focussed with convex lens optics, to pass through the reactor via two a circular metallic optical stops (32 mm diameter) that were fitted externally in front of the quartz windows of the reactor (Fig. 1). A variable-speed magnetic stirrer was placed beneath the thermostat to maintain the charge of powdered photocatalyst in suspension. The entire experimental arrangement was mounted firmly on an optical bench and enclosed within a protective wooden container to shield the exterior from extraneous UV radiation. The reactor body was fitted with a septum through which liquid samples (1 cm^3) were withdrawn using a glass syringe for centrifugation, and then analysis by gas–liquid chromatography in 20 μl aliquots.

The UV radiation entered the reactor through one quartz window, and photons not absorbed within the reactor body were monitored upon exiting through the second window with one of the three devices; a spectro-radiometer (Bentham Instruments), a broad band-width photovoltaic cell, or a chemical actinometer containing tri-potassium tris-oxalato iron (III) solution.

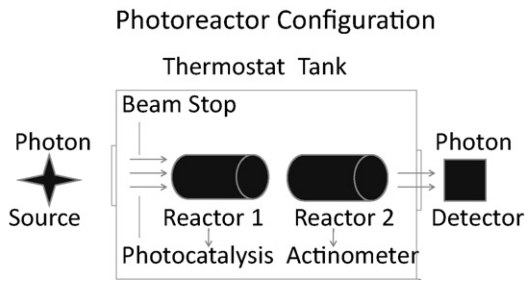

Fig. 1. Schematic diagram of the photoreactor.

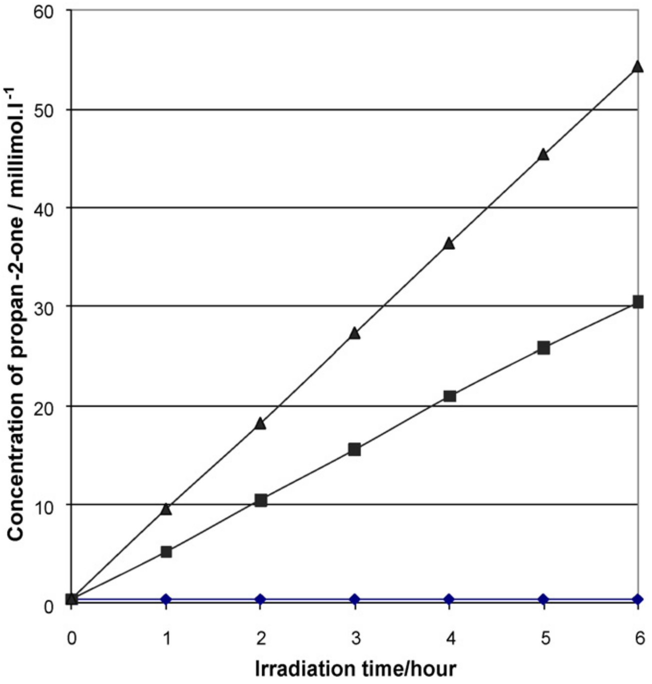

Fig. 2. Effect of di-oxygen partial pressure on the rate of formation of propan-2-one. Pure argon (♦), dry air (■), pure di-oxygen (▲), each at atmospheric pressure. TiO$_2$ loading of 750 mg l^{-1} (for details of values of zero-order slopes (^{o}k) and intercepts (c_o), see Table 1).

2.2. Materials

TiO$_2$ specimens; P25 (ex-Degussa, Germany and Japan), Pure Anatase (ex-Merck and Tioxide), Pure Rutile (LAR) (ex-Tioxide). Propan-2-ol[1] and Propan-2-one (Spectroscopic Grades, ex-Aldrich, 99.5%). Argon and di-oxygen cylinder gases (ex-Air Products).

3. Results

Fig. 2 summarises the manner in which propan-2-one is formed during the photocatalysis, at 24 °C. It is expressed in terms of concentration/time plots, corrected for the presence of residual propan-2-one, under three different reaction conditions using a fixed dispersion concentration of P25 of 750 mg l^{-1} but with variations in the gas phase composition above the liquid; pure argon, air passed through a column of outgassed molecular sieve (Linde 13X),

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[1] Propan-2-ol contained $\leq$0.002% of propan-2-one as a residual impurity.

Table 1
Zero-order rate constants (${}^{o}k$) of formation of propan-2-one over various preparations of TiO_2 shown in the integrated form of the rate expression: $c_t = {}^{o}kt + c_o$.

Specimen	BET area/m^2 g^{-1}	10^4 ${}^{o}k$ (mol l^{-1} h^{-1})	10^4 c_o (mol l^{-1})
P25 J (O_2)	41	91.3	5.4
P25 G (O_2)	39	89.2	7.8
P25 G (air)	39	50.0	5.0
P25 G (argon)	39	0.0	4.0
Rutile (LAR) (O_2)	4	1.8	<0.1
Merck anatase (O_2)	6	4.6	<0.1

Photocatalyst loadings: 750 mg l^{-1}.

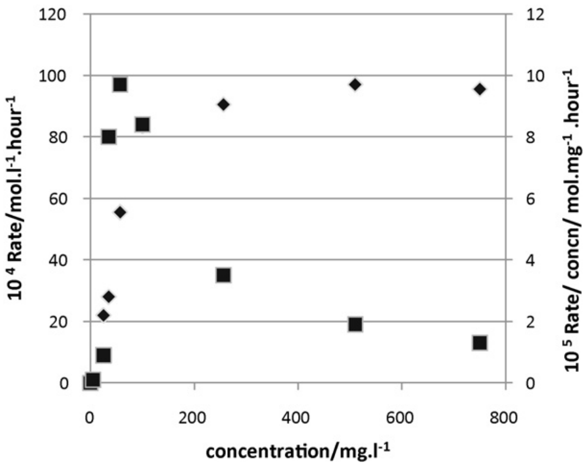

Fig. 3. Rate of formation of propan-2-one (♦) (left ordinate) and rate of formation of propan-2-one/dispersion concentration (■) (right ordinate) as functions of the P25 photocatalyst dispersion concentration (abscissa); $p_{O_2} = 1$ atmosphere, 24 °C.

or pure di-oxygen; each gas at atmospheric pressure, and sparged for 15 min through the propan-2-ol before use.

Table 1 presents rate data for several photo-catalysts, each at a fixed concentration of 750 mg l^{-1}, using pure di-oxygen at atmospheric pressure and 24 °C, which illustrates a large degree of reactivity variability. For one of these photo-catalysts, Fig. 3 shows the variations in rate of photo-oxidation (primary ordinate) as a function of the P25 TiO_2 dispersion concentrations (abscissa), and also the variations of the rate, expressed per unit dispersion concentration (secondary ordinate).

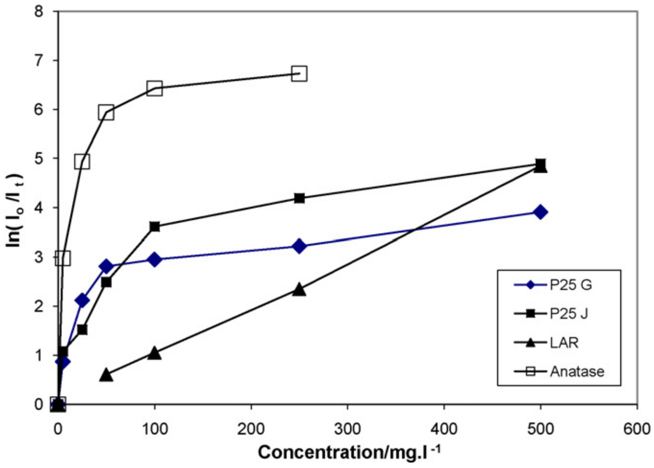

Fig. 4. Beam Intensity Attenuation ($\ln(I_0/I_t)$) (ordinate) with dispersion concentration (abscissa) for different TiO_2 photocatalysts. P25 G (♦), P25 J (■), Anatase (□), low area rutile (LAR) (▲).

Table 2
Quantum efficiencies (φ) versus P25 dispersion concentration.

Dispersion concentration (mg l^{-1})	Beam attenuation (%)	Quantum efficiency (φ)
5	58	0.01
25	88	0.36
50	94	0.84
250	96	1.4
500	98	1.4
750	>99	1.3

Incident beam flux (I_o) (photon s^{-1}) = 2.4 ± 0.1 × 10^{17}. Peak input of power of source (mW) (at λ = 365 nm) = 105 ± 5.

Accompanying the rate data are presented, in Fig. 4, results showing the extents to which the incident UV beam is attenuated as a function of the dispersion concentration for three different photocatalysts, in the form of Beer–Lambert plots ($\ln(I_0/I_{trans})$) versus dispersion concentration. Additionally, Table 2 presents data which reveal the combined effects of the dispersion concentration upon both the proportion of the beam flux that is absorbed within the reactor, and upon the quantum efficiency of the corresponding rate process.

4. Discussion

Fig. 2 reveals firstly, that upon exposing the reaction mixture to the incident beam in the absence of an oxidising gas (air or pure oxygen), a limited additional amount of propan-2-one (4×10^{-4} mol l^{-1}) appears in the liquid phase, but the reaction is seemingly unsustainable in the absence of either air or di-oxygen, and notably the photocatalyst darkens perceptibly [9], through the loss of surface oxide species. Secondly, the rate of evolution of propan-2-one, in the presence of both air and gaseous di-oxygen, is strictly of zero-order throughout the periods in which its progress was followed, but shows a marked pressure-dependency ($p^{n}_{O_2}$, $n < 1$), the reaction rate with filtered air being significantly reduced to 56% relative to the rate in pure di-oxygen. This variability of rate with di-oxygen pressure indicates clearly that the uptake of molecular di-oxygen by the partially reduced titania surface is the rate-determining step under these conditions. A similar pressure-dependency was previously observed by Vishwanathan [10] in a study of the photo-adsorption of gaseous di-oxygen at hydroxylated titania surfaces, at much lower pressure values ($p_{O_2} <$ ca. 0.001 bar) suggesting that the rate controlling steps in both cases relate to di-oxygen uptake. A further factor, evident as a consequence of the strict linearity of the evolution of propan-2-one with irradiation time, is that extrapolation of the lines to zero irradiation time yields small positive intercepts (c_o in Table 1) particularly with the highest surface area solid ranging from 5.0 × 10^{-4} to 7.8 × 10^{-4} mol l^{-1}. The intercepts are much smaller with the lower specific area solids, probably due in part to their lower surface areas, and additionally to their reduced reactivities per unit mass, which can be correlated with a smaller degree of reduction (x). Thus upon exposing the reaction mixture to the incident UV beam, a surface reaction is initiated between strongly adsorbed propan-2-ol [11] and activated lattice oxygen species, which leads to the oxidation of the adsorbed alcohol, and the concurrent reduction of the titania lattice. The latter process results in an upwards shift in the Fermi level of the solid that discourages electron-hole separation within the space-charge layer, and causes a reduction in the rate at which propan-2-one is released into the liquid phase. Thus the photo-oxidation rate initially appears to decrease towards a steady-state, while simultaneously the reduction rate of molecular di-oxygen increases until it stoichiometrically balances the steady-state value of the former process; this characteristic being clearly observable as an induction period of a few minutes duration in a manometric study by the author of UV-induced di-oxygen uptake on TiO_2 surfaces that had been pre-saturated with a monolayer of strongly adsorbed propan-2-ol [12].

At a fixed value of the dispersion concentration (750 mg l^{-1}), selected to completely attenuate the incident photon beam within the reactor, different photocatalytic materials display (Table 1) a range of activities (each of zero-order) from the smallest of 1.8×10^{-4} mol l^{-1} h^{-1} for a low specific area rutile specimen (LAR) to the largest (92 and 89×10^{-4} mol l^{-1} h^{-1}) for two independently manufactured specimens of P25; the latter aspect suggesting that its wide availability could favour its use as a standard photocatalytic material, despite there being difficulties in assigning an accurate structural characterisation to it. The difference between the measured rate constants of the P25 materials probably arises from the small difference in their specific areas, and the limitations of experimental accuracy overall. It is well-known that P25 is bi-phasic, with the anatase and rutile phases present approximately in the ratio 80/20 [13], but some uncertainty remains concerning the relative dispositions of the two phases within the assembly of particles; namely, as separate particles of pure rutile and pure anatase in the appropriate ratio, or as individual particles that are partially converted from pure anatase into rutile, the latter phase being thermodynamically the more stable in the bulk state [14,15].

The variation of the rate of photo-oxidation of propan-2-ol as a function of the catalyst dispersion concentration (Fig. 3) increases from small values at the lower concentrations, before maximising, and then undergoing a small decline of ca. 5% at the highest loading.

However the rate, when expressed per unit dispersion concentration shows complex behaviour that commences with steep increases in value at low concentrations before attaining a maximum and then declining markedly at concentrations greater than the maximum.

These characteristics are explicable by reference to information displayed in Table 2 and Fig. 4. Table 2 reveals that at low dispersion concentrations, the experimentally determined quantum efficiencies of the reaction are small, suggesting a dominance of electron-hole recombination [16] but they increase to values greater than one as the concentration rises; such values of quantum efficiency ($\varphi > 1$) have been reported previously for other photocatalytic processes [17,18]. The basis of some values of φ being greater than unity may quite possibly arise from the present experimental arrangement, which facilitates the continuous exchange of particles between a smaller irradiated region and the remaining, much larger, dark region of the reactor, that may temporarily enable a reversal of the detrimental influence of surface photovoltage on the magnitude of the electric field across the space-charge layer. In the current set of experiments the values of φ in excess of one are considered to be due to active oxidising species also being created during the thermal-reduction of dissolved di-oxygen, in addition to those formed directly by hole capture. It seems also that the di-oxygen reduction step has a temperature dependency [19]. Secondly, Fig. 4 reveals that low area rutile particles conform with a Beer–Lambert relationship over a wide variation of dispersion concentration, whereas P25 TiO_2 exhibits more complex behaviour, commencing with Beer–Lambert (B–L) compliance at lower concentrations, which then transforms into a different beam attenuation characteristic above a critical concentration value of ca.50 mg l^{-1}; similar behaviour being observed with monochromatic UV radiation of 365 nm wavelength. This transition, which appears to occur below the concentration at which the maximum rate is attained, suggests, that above this critical concentration, the structure of the dispersion is no longer the same as it was below it, the accompanying slope of the B–L plot implying characteristics attributable to a suspension of much greater average particle size, which would occur if particle aggregation commenced at this transition point, with the additional attenuation being contributed by the larger particles, while the remainder of the effect continues to be provided from well-dispersed material. It is not a case of all of the smaller particles participating in this structural transformation, but simply the excess above the critical value.

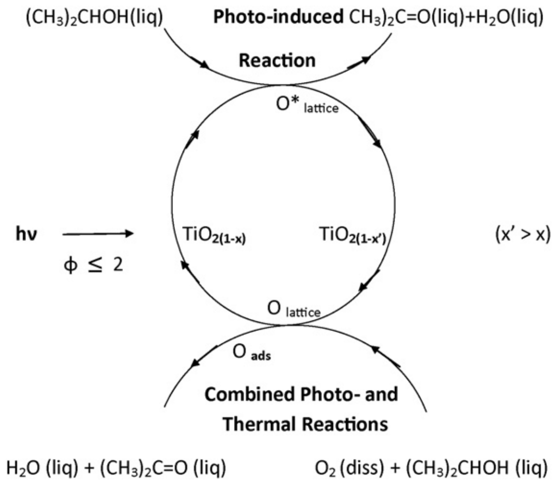

Fig. 5. Diagrammatic summary of the photocatalytic reaction mechanism depicting the photocatalytic oxidation of propan-2-ol coupled with the photo- and thermal re-oxidation of the photo-reduced titania.

By proposing these features, it is possible to account for the subtle changes that appear in the variation of the rate per unit dispersion concentration as a function of the dispersion concentration (Fig. 3). At small values, the initial upwards curvature of the plot is due mainly to increases in the quantum efficiency of the reaction as the absorbed energy density per particle gradually diminishes, and to the increasing numbers of individual particles attenuating the photon beam. The maximum in the curve is principally created by two factors which oppose the increase; namely, the postulated growth in average particle size from the agglomeration of an increasing proportion of the dispersed phase, which will tend to lower the value of the rate per unit dispersion concentration as it becomes more dominant, plus the influence of dispersed material in excess of that necessary for the complete attenuation of the incident photon beam within the reactor volume; this latter behaviour would progressively confine the beam into a smaller fraction of the reaction path-length, and effectively constrict the reaction volume to the vicinity of the window upon which the incident beam impinges. The fact that the measured rate of photo-oxidation remains fairly constant throughout these changes is consistent with the process now being photon flux limited, so that any attempt to increase the rate of reaction, other than by increasing the photon flux, will be unsuccessful. Whether an increase of rate would be pro rata, or otherwise, cannot be inferred from the present investigation, but variations in reaction rate as a result of variations in the incident photon flux have been shown for this process previously [7,16]. Hence by increasing the gaseous di-oxygen pressure in contact with the liquid propan-2-ol – P25 dispersion from 1 to ca. 5 bar does not lead to an increase in the rate (J.-M. Herrmann, Private Communication, 2009), even though it is quite clear, from the pressure-dependency at pressures below 1 bar, that the uptake of di-oxygen by the photocatalyst is rate controlling in those conditions. A mechanistic summary of the photocatalytic process is provided diagrammatically in Fig. 5, depicting a two-stage process; the photo-induced oxidation of propan-2-ol to propan-2-one with the concurrent reduction of the titania photocatalyst, coupled with the re-oxidation of the photo-reduced titania; the latter stage being attributed mainly to stimulation by thermal activation in the present system configuration, although photo-induced oxidation has been demonstrated when thermally reduced titania was irradiated with near UV at 25 °C in the presence of gaseous di-oxygen [10], and by implication must also be present.

5. Conclusions

The zero-order rate of propan-2-ol photo-oxidation to propan-2-one provides a reliable means of comparing its reaction characteristics with those of other processes, in systems that are not necessarily constructed in identical ways, nor which use identical UV sources. What is also clear from the use different photocatalytic materials is that the optical characteristics of the dispersions may change as a result of them undergoing concentration-dependent structural changes, so that the photocatalyst concentration conditions themselves require careful definition if the comparison is to be strictly meaningful, and, in whatever those circumstances are, the beam attenuation should be complete within the reactor volume. Constant temperature conditions are also necessary since the reaction rate has been shown to possess a small temperature coefficient, and variations of temperature may further alter the stability of agglomerated solids, and their influence upon the overall quantum efficiency of the photocatalytic process.

Alternative standard reactions have also been proposed based on the decolourisation of dyestuffs. What is evident however is that similar concentration-dependent changes to the structure of the TiO_2 photocatalyst dispersion are likely to obtain, and similar arguments concerning the definition of the dispersion concentration for this standard process are probably as relevant as they appear to be for propan-2-ol photo-oxidation. Additionally, it is likely that the zero-order propan-2-ol photo-oxidation to propan-2-one is less susceptible to problems arising from competitive adsorption of products than may be anticipated for dyestuff decolourisation, in which the coloured reagent is much less strongly adsorbed.

Acknowledgements

I wish to dedicate this presentation to the memory of (the late) Professor Mario Schiavello (DICPM, University of Palermo), whose friendship, counsel, interest and encouragement prevailed since we became acquainted as post-doctoral workers in Professor F.S. Stone's laboratory in the University of Bristol, almost 50 years ago.

I also wish to thank the University of Bradford for their continuing support; to Ms. A.T. Costigan, Subject Specialist Librarian, for her endeavours in establishing an historical perspective of the development of the subject of photocatalysis, to my former co-workers, Drs. L.T. Hogg, V. Vishwanathan and R.K.M. Jayanty, and to the EPSRC for their financial support.

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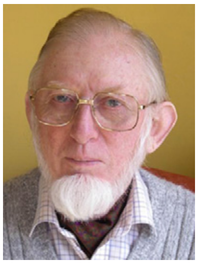

Roger Bickley obtained the doctoral degree of PhD in Physical Chemistry at the University of Exeter (UK) under the direction of the internationally respected Surface Chemist, Professor S.J. Gregg. In 1962, as a young post-doctoral worker in Professor F.S. Stone's laboratory in the University of Bristol, he began to work upon light-induced surface processes, photosorption and photocatalysis; topics in which he has maintained a strong interest while working at the University of Bradford, where he now holds the post of Honorary Visiting Senior Lecturer in Physical Chemistry. In addition to his photocatalytic studies, he has studied high temperature reactions of metals and alloys with oxidising gases and vapours; solid state chemistry including phase transformations of solids, and the electroless deposition of nickel-phosphorus alloys on ferrous materials. He has published many research papers, and been the author of several review articles. He has lectured in many countries, and participated in several large international research projects. Although now officially retired he continues to remain academically research active.