Catalysis Letters 4 (1990) 345–354

KINETICS OF THE GAS-SOLID HETEROGENEOUS PHOTOCATALYTIC OXIDATION OF TRICHLOROETHYLENE BY NEAR UV ILLUMINATED TITANIUM DIOXIDE

Lynette A. DIBBLE ** and Gregory B. RAUPP *

Department of Chemical, Bio & Materials Engineering, Arizona State University, Tempe, Arizona 85287-6006, U.S.A.

Received 4 October 1989; accepted 16 February 1990

Ultraviolet heterogeneous photocatalysis, oxidation, trichloroethylene, titania, kinetics

Kinetics of the gas/solid heterogeneous photocatalytic oxidation of dilute trichloroethylene (TCE) vapors by ultraviolet-illuminated titanium dioxide have been determined using a fixed-bed dynamic photoreactor. Reaction rate dependences on inlet TCE, oxygen and water vapor concentrations were found to consist of both reactant sensitive and insensitive regions. In the reactant sensitive regions, measured limiting apparent reaction rate orders for TCE, oxygen and water vapor are 0.8, 1.7 and -3, respectively. Water vapor in the reactant stream lowers *initial* reaction rates relative to corresponding water free conditions, but is required to sustain photocatalytic activity for extended periods of time.

1. Introduction

Novel processes based on photocatalyzed reactions with semiconducting powders such as titanium dioxide show great promise for rapid, efficient destruction of environmental pollutants that have proven difficult or expensive to treat using established remediation methods [1–7]. The ability of ultraviolet (UV) illuminated titanium dioxide to effect the partial and complete oxidation of gaseous paraffins, olefins and alcohols is well documented [8–14]. Most efforts to apply photoassisted reactions to the destruction of environmental contaminants have focused on purification of aqueous solutions in *slurry* reactors using relatively intense levels of ultraviolet light [15–18]. In contrast, we have focused on *gas-solid* heterogeneous photocatalyzed oxidation of *vapor-phase* contaminants using relatively low levels of ultraviolet light energy.

Trichloroethylene (TCE) was chosen as the test compound for this research since it has been the subject of previous extensive work in slurry phase reactors

---

* Author to whom correspondence should be addressed.

** Present Address: University of Wisconsin, Water Chemistry Program, Madison, WI, 53706, U.S.A.

[15,19] and because it is a pollutant of great environmental concern. Among all synthetic organic contaminants detected in domestic public drinking water supplies, none occur more frequently or at higher concentrations than trichloroethylene [20]. As a consequence, TCE is a major gas-phase contaminant of water treatment facility effluents (e.g., air from stripping towers and activated carbon regeneration). The need for effective air pollution remediation technology for such facilities is expected to become more critical as emissions of volatile organics into the atmosphere become more tightly regulated.

We have successfully demonstrated the destruction of dilute levels of gaseous trichloroethylene in various gas carrier streams by near-UV illuminated titanium dioxide powder [7]. This paper reports the results of experiments to determine the intrinsic reaction rate dependence on trichloroethylene, oxygen and water vapor concentrations.

2. Experimental

Figure 1 is a schematic diagram of the experimental TCE photocatalytic oxidation kinetics apparatus. Mass flow controllers (Tylan) deliver trichloroethylene (474 ppm, balance nitrogen, Matheson), oxygen (109 ppm and 21 percent O_2, balance nitrogen, Liquid Air) and ultra-high purity nitrogen (99.999%, Liquid Air) from compressed gas cylinders. Controlled amounts of water vapor are introduced by bubbling nitrogen through a glass saturator containing nitrogen-stripped distilled, deionized water. Water content is determined by the nitrogen flow rate and the saturator temperature. The fixed bed dynamic photoreactor,

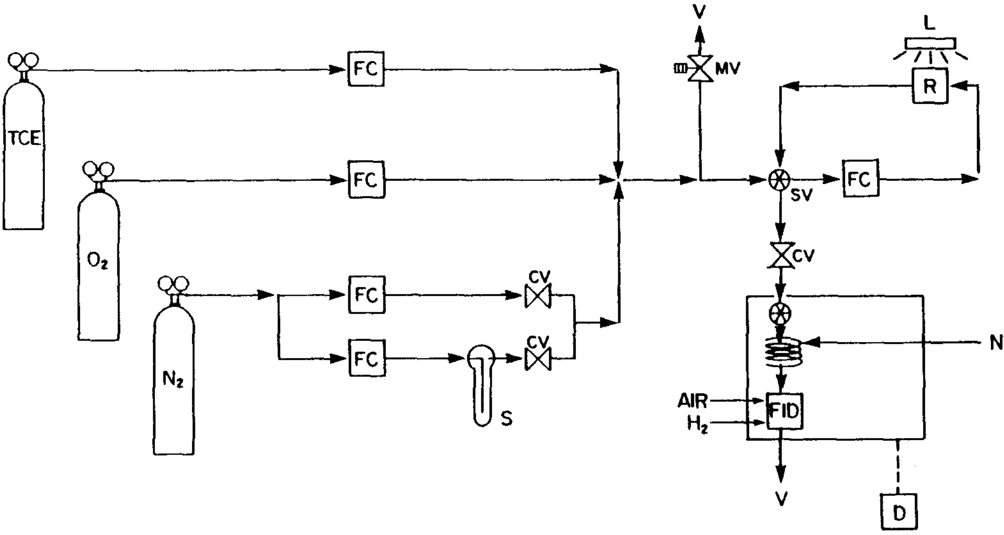

Fig. 1. Schematic of the experimental apparatus. CV: check valve; D: data collection; FC: flow controller; L: UV light; MV: metering valve; R: reactor; S: saturator; SV: sampling valve; V: vent.

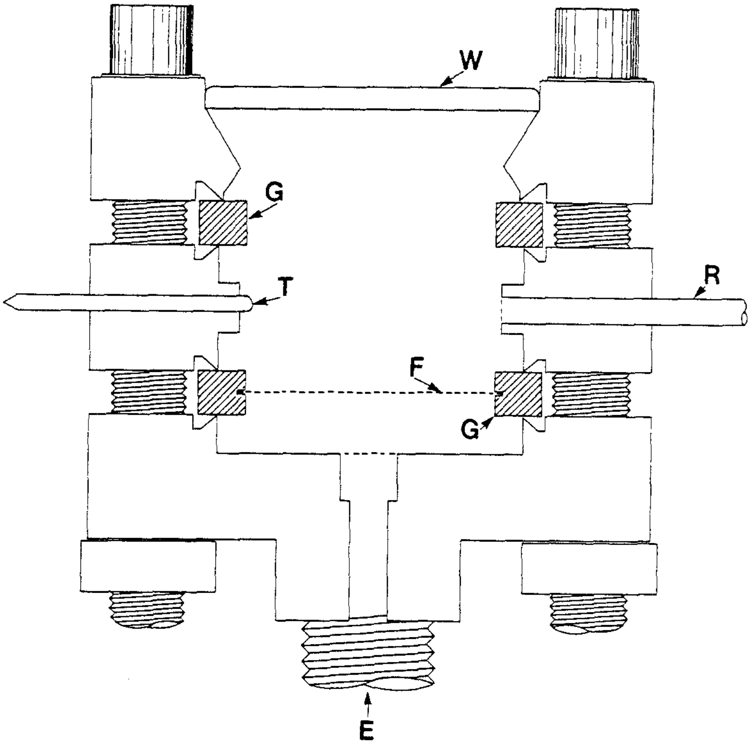

Fig. 2. Fixed bed dynamic photoreactor. E: effluent line; F: filter support; G: teflon gaskets; R: reactant inlet; T: thermocouple; W: window.

sketched in cross section in fig. 2, was constructed from stainless steel flanges (Huntington) equipped with knife edge seals and a zero-length viewport of 7056 optical quality pyrex glass (Larson Electronic Glass). This window acts as a filter by transmitting only light wavelengths greater than 300 nm, with 90% transmission at $\lambda \geq 350$ nm (see fig. 3). The reactor flanges are sealed with Teflon gaskets. Powdered titanium dioxide catalyst (anatase, Aldrich) is spread in a thin layer on a paper filter, the edge of which is inserted into a thin slit cut into the bottom gasket. A type "J" iron-constantan thermocouple monitors the temperature of the reactor cavity above the catalyst bed.

A four watt fluorescent "black light" bulb (GE F4T5-BLB) illuminates the catalyst bed. The light flux entering the reactor was determined to be 4.1×10^{-9} Einsteins/cm^2-s by potassium ferrioxalate actinometry [21]. This intensity level is approximately three orders of magnitude lower than the light flux used in slurry phase mineralization of TCE solutions [15,19]. The output spectrum of the light source, shown in fig. 3, is primarily in the near ultraviolet, and corresponds to the excitation region of titanium dioxide.

The illuminated reactor cavity volume is 3.14 cm^3 and the illumination surface area of the filter is 2.09 cm^2. Reactor effluents flow continuously from the reactor

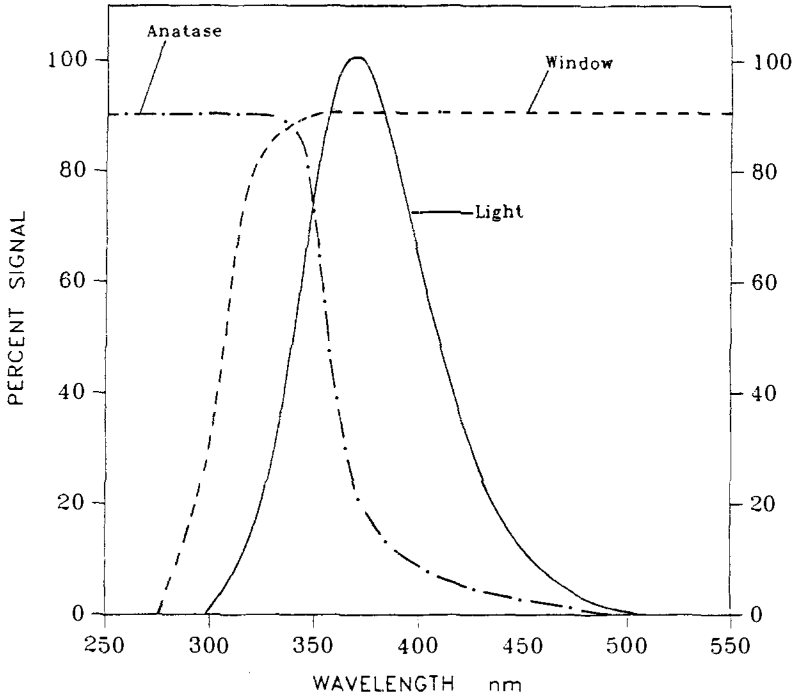

Fig. 3. Comparison of near UV transmission of reactor window glass [22], relative spectral output of UV source [23] and anatase absorption spectrum [9].

to the sampling loop (0.5 cm^3) of a chromatographic valve. A Varian 3700 gas chromatograph equipped with a flame ionization detector and a 0.1% SP-1000/Carbopack C column (Supelco) analyzes discrete samples of the reactor effluent.

In a typical experiment, approximately 56 mg of untreated catalyst was spread in a thin layer on the filter and the reactor was sealed. Reactant flow rates were set at their desired values and a portion of this mixture (20–100 cm^3/min) was delivered to the reactor. After steady conditions had been established as determined by the TCE output signal, the ultraviolet light was switched on and reactor effluent samples were analyzed until a constant TCE concentration from the reactor was once again recorded. Steady state TCE consumption rates R (μmol TCE/gm-min) were calculated assuming ideal gas behavior as follows:

$$R = (QP/wRT)[C_{in} - C_{out}], \tag{1}$$

where

Q = volumetric reactor feedrate, sccm
P = reactor total pressure, 1.1 atm
w = mass of catalyst bed, gm
R = gas constant, 8.205×10^{-5} cm^3-atm/μmol-K
T = reactor temperature, K

C_{in} = TCE concentration at inlet, μmol TCE/μmol total
C_{out} = TCE concentration at outlet, μmol TCE/μmol total.

Experiments in the absence of ultraviolet illumination with catalyst and under UV illumination in the absence of catalyst were performed to rule out TCE conversion due to homogeneous and non-photoassisted reactions. Standard diagnostic tests were performed over the full range of conditions to rule out intrusion of external mass transfer effects on our reaction rate measurements. Operation of the photoreactor at flowrates above ca. 10 cm^3/min resulted in reaction rates which were essentially free of mass transfer limitations.

Reactant conversions were estimated assuming that the stoichiometry for the trichloroethylene oxidation is as proposed by Pruden and Ollis [15] for mineralization of TCE in a slurry reactor:

$$Cl_2C = CHCl + \tfrac{3}{2}O_2 + H_2O \xrightarrow[TiO_2]{h\nu} 2CO_2 + 3HCl. \qquad (2)$$

In our experiments no organic reaction products resulting from partial oxidation reactions were detected. The presence of hydrogen chloride could not be determined quantitatively, but qualitative evidence for HCl production was seen in the slight dulling typical of acid attack on the stainless steel reactor walls downstream of the catalyst bed. Carbon dioxide was detected in separate in situ infrared spectroscopy experiments. In the absence of further evidence, we assume that the stoichiometry represented in eq. (2) also holds for the gas-solid photocatalytic reaction. Most limiting reactant conversions were below 10%. However, maximum flowrate limitations precluded the constraint of differential conversion under certain conditions. Estimates of Peclet numbers under typical experimental conditions suggest that flow behavior is well-mixed, and hence reaction rates are correlated with outlet reactant concentrations.

3. Results and discussion

Figures 4–6 show the dependences of TCE photocatalytic oxidation rate on TCE, oxygen and water vapor concentrations, respectively. Each plot shows two distinct regions: one in which reaction rates are insensitive to reactant mole fractions and a second showing a nonzero linear relationship between log reaction rate and log concentration (mole fraction). These two regions are connected by a gradual transition zone extending over a significant portion of the abscissa. This behavior is typical of that exhibited by heterogeneous reactions. The location of the transition regime is a function of coreactant concentrations, as shown for water vapor in fig. 6. In the reactant sensitive regions, reaction rates show a positive correlation with trichloroethylene and oxygen mole fractions and a negative correlation with water vapor mole fraction. If we assume that in the

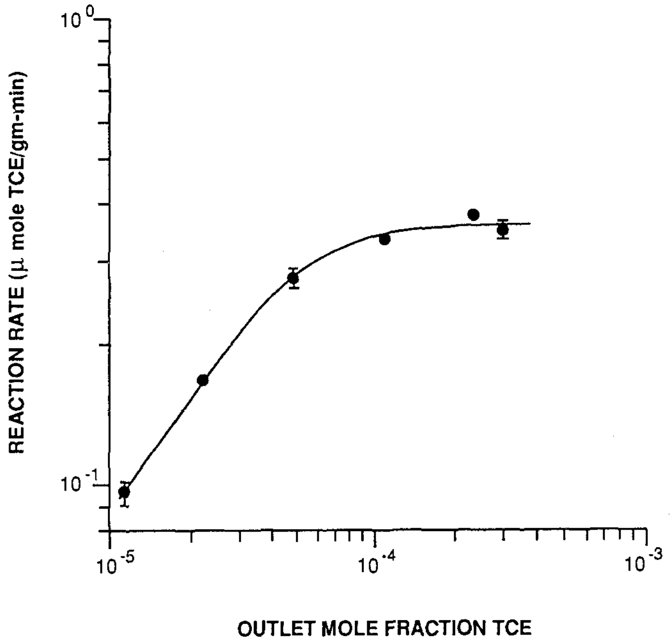

Fig. 4. TCE oxidation rate as a function of outlet TCE mole fraction. O_2 mole fraction $=1.47\times10^{-2}$, H_2O mole fraction $=8.4\times10^{-3}$.

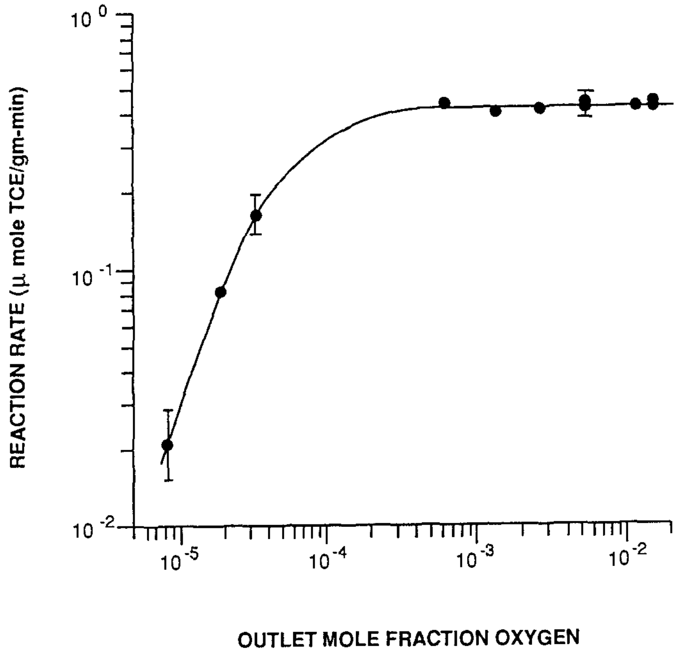

Fig. 5. TCE oxidation rate as a function of outlet oxygen mole fraction. TCE mole fraction $=1.89\times10^{-4}$, H_2O mole fraction $=8.5\times10^{-3}$.

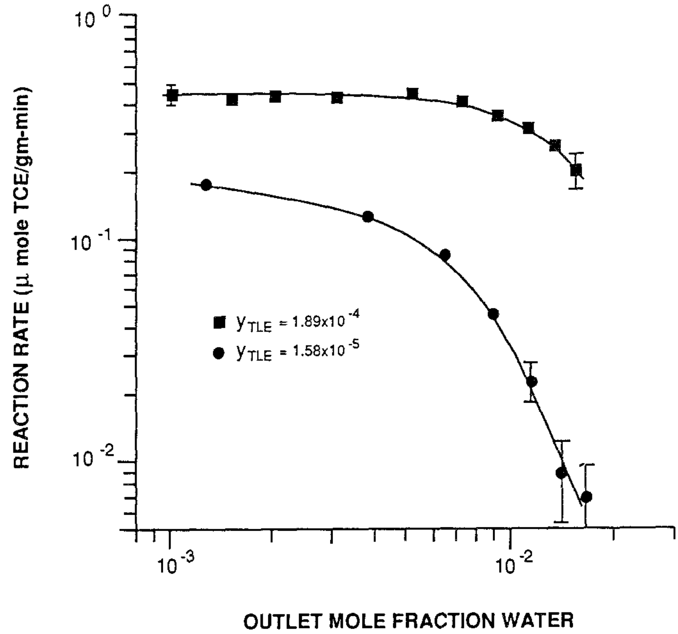

Fig. 6. TCE oxidation rate as a function of outlet water vapor mole fraction for two TCE levels. O_2 mole fraction $= 1.17 \times 10^{-3}$.

reactant sensitive regimes the reaction rate R depends on reactant mole fraction y_i according to the following empirical power law forms:

$$R = k_1 y_{\mathrm{TCE}}^{\alpha}, \quad R = k_2 y_{\mathrm{O_2}}^{\beta}, \quad R = k_3 y_{\mathrm{H_2O}}^{\gamma}, \tag{3}$$

the figures yield limiting slopes $\alpha = 0.8 \pm 0.2$, $\beta = 1.7 \pm 0.4$ and $\gamma = -3.3 \pm 0.9$. The empirical rate parameters k_1 and k_2 are independent of coreactant concentrations, but k_3 contains an implicit dependence on TCE and oxygen concentration. The reaction rate is also a function of light intensity. Because light intensity was held at a constant level during all experiments, this dependence is contained in the reaction rate parameters and has not been quantified.

Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate forms can be used to describe reaction rates which exhibit shifts in apparent order. The rate expression given by

$$R = k'\left\{\frac{K_1 y_{\mathrm{TCE}}}{1 + K_1 y_{\mathrm{TCE}} + K_3 y_{\mathrm{H_2O}}}\right\}\left\{\frac{K_2 y_{\mathrm{O_2}}}{1 + K_2 y_{\mathrm{O_2}} + K_4 y_{\mathrm{H_2O}}}\right\}^2 \tag{4}$$

describes reaction rate concentration dependences which shift from first to zero order in TCE with increasing TCE concentration, from second to zero order in oxygen with increasing oxygen concentration, and from zero to negative third order in water vapor with increasing water concentration. Although *limiting* forms of expression (4) are consistent with our kinetic results, attempts to fit the data to this form over the entire set of experimental conditions were not successful. If rate parameters are adjusted to achieve a good prediction of TCE and oxygen concentration dependences, a sufficiently severe negative dependence on water vapor concentration cannot be realized at high water vapor concentrations, since under these conditions the overall rate exhibits a finite positive dependence on TCE and O_2 concentrations. However, by using the following modification of expression (4):

$$R = k'\left\{\frac{K_1 y_{\mathrm{TCE}}}{1 + K_1 y_{\mathrm{TCE}} + K_3 y_{\mathrm{H_2O}}}\right\}\left\{\frac{K_2 y_{\mathrm{O_2}}/y_{\mathrm{H_2O}}}{1 + K_2 y_{\mathrm{O_2}}/y_{\mathrm{H_2O}} + K_4 y_{\mathrm{H_2O}}}\right\}^2 \tag{5}$$

a sufficiently strong water dependence is predicted and good agreement is found between experimental and predicted reaction rates over the entire range of data. Other rate expressions may exist which are capable of describing the observed rate behavior as well or better than expression (5). Further parameter fitting coupled with mechanistic studies must be performed to establish a valid reaction rate expression.

These experiments have established the importance of all three reactants (TCE, oxygen, water vapor) for the *sustained* photocatalytic oxidation of trichloroethylene. No appreciable reaction takes place in the absence of oxygen. Although *initial* reaction rates with water free reactant streams and fresh (well hydrated) titanium dioxide are substantially higher than those that can be achieved with humid reactant streams, catalytic activity decreases dramatically after only a few minutes of irradiation and eventually becomes negligible. In contrast, catalytic activity achieved under humid conditions can be sustained indefinitely. The need for water is not surprising in light of the fact that a stoichiometric reaction for complete TCE oxidation in which both HCl and CO_2 are produced cannot be written using only O_2 or H_2O as the oxidant.

The observed decrease in activity upon addition of water to the reactor feed could be due to the following effects: (i) competition between water molecules and other reactants or intermediates for active surface sites, and/or (ii) an increase in the illuminated semiconductor electron-hole recombination rate due to the loss of surface hydroxyl hole traps from dissociative water adsorption. Water vapor does not absorb in the near UV, so it is unlikely that the activity decrease is due to light attenuation. It is interesting to note that many of the gas/solid hydrocarbon photoreactions cited in the introduction of this paper were accomplished in the absence of water vapor. In much of that work (e.g., oxidation of chlorobenzene or chloromethane) water is a product of the reaction, and is not required as a reactant.

Under ambient conditions, titania surfaces are covered with a substantial layer of adsorbed water that significantly affects photocatalytic activity [10,24]. It appears that under conditions in which water vapor is not fed to the reactor, water required by the stoichiometric reaction could be temporarily provided by these adsorbed water molecules or hydroxyls from dissociative adsorption of water on the TiO_2 surface. Indeed, titanium dioxide placed overnight in a dessicator became inactive for this reaction; subsequent exposure of this dehydrated titanium dioxide to streams containing water vapor only slightly improved the catalytic activity. Literature results show that such mild treatment might remove adsorbed surface water, but not hydroxyl groups [25–27]. Surface pretreatment is therefore critical in determining catalytic activity.

The role of water in this reaction is only one of the questions that must be examined before a mechanism describing the gas/solid photocatalytic oxidation of TCE over near-UV illuminated TiO_2 can be proposed. Other factors which warrant study include the nature of TCE adsorption on hydroxylated and dehydroxylated titania, the changes in reactant adsorption upon exposure to ultraviolet light, the nature and role of intermediate (transient) species and the desorption/adsorption behavior of reaction products. To address these questions, we have designed a photoreaction cell which allows simultaneous irradiation of titanium dioxide powders by infrared and ultraviolet light; in situ experiments utilizing transmission infrared spectroscopy of the photocatalyst during reaction are now underway in our laboratory.

Acknowledgements

This work was supported by the Arizona State University Research Fund, the ASU Graduate Student Association Research Development Program and Sigma Xi. One of us (LAD) gratefully acknowledges the Phelps-Dodge Corporation for providing a graduate fellowship.

References

[1] J.J. Carey, J. Lawrence and H. Tosine, Bulletin of Environmental Contamination and Toxicology 16 (1976) 697.
[2] S. Frank and A. Bard, J. of Phys. Chem. 81 (1977) 1484.
[3] D. Ollis, Environmental Science and Technology 17 (1983) 628.
[4] R. Matthews, Water Research 20 (1986) 569.
[5] B. Oliver and J. Carey, *Homogeneous and Heterogeneous Photocatalysis*, eds. E. Pelizzetti and N. Serpone (D. Reidel Publishing, Dordrecht, Holland, 1986) pp. 629–650.
[6] C. Grätzel, M. Jirousek and M. Grätzel, J. Molec. Catal. 39 (1987) 347.
[7] L. Dibble and G. Raupp, *Proc. Arizona Hydrological Society, First Annual Symposium*, Sept. 16–17, Phoenix, AZ, 1988, pp. 221–229.
[8] I. McLintock and M. Ritchie, Transactions of the Faraday Society 61 (1965) 1007.
[9] M. Formenti, F. Juillet, P. Meriaudeau, P. and S. Teichner, ChemTech 1 (1971) 680.
[10] R. Bickley, G. Munuera and F. Stone, Faraday Discussions of the Chemical Society 58 (1974) 194.

[11] N. Djeghri, M. Formenti, F. Juillet and S. Teichner, Faraday Discussions of the Chemical Society 58 (1974) 185.

[12] P. Pichat, J. Hermann, H. Courbon, J. Disdier and M. Mozzanega, Can. J. of Chem. Eng. 60 (1982) 27.

[13] S. Teichner and M. Formenti, *Photoelectrochemistry, Photocatalysis and Photoreactors*, ed. M. Schiavello (D. Reidel Publishing, Dordrecht, Holland, 1985) pp. 457–489.

[14] N. Blake and G. Griffin, J. Phys. Chem. 92 (1988) 5697.

[15] A. Pruden and D. Ollis, J. Catal. 60 (1983) 404.

[16] D. Ollis, C. Hsiao, L. Budiman and C. Lee, J. Catal. 88 (1984) 89.

[17] H. Al-Ekabi and N. Serpone, J. Phys. Chem. 92 (1988) 5726.

[18] R. Matthews, J. Catal. 113 (1988) 549.

[19] S. Ahmed and D. Ollis, Solar Energy 32 (1984) 597.

[20] J. Dyksen and A. Hess, J. American Water Works Association 74 (1983) 394.

[21] J. Calvert and J. Pitts, *Photochemistry* (John Wiley and Sons, New York, 1966) pp. 783–786.

[22] *Larson Electronic Glass Catalogue* (Redwood City, California, USA).

[23] W. Elenbas, ed., *Fluorescent Lamps and Lighting* (MacMillan Company, New York, 1959) p. 150.

[24] A. Boonstra and C. Mutsaers, J. Phys. Chem. 79 (1975) 1694.

[25] K. Lewis and G. Parfitt, Transactions of the Faraday Society 62 (1966) 204.

[26] P. Jackson and G. Parfitt, Transactions of the Faraday Society 67 (1971) 2469.

[27] G. Munuera, V. Rives-Arnau and A. Saucedo, J. Chem. Soc., Faraday Transactions I, 75 (1979) 736.